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The distribution of certain elements among coexisting calcic pyroxenes, calcic amphiboles and biotites in skarns

R. KRETZ
Geological Survey of Canada, Ottawa, Canada

(*Received* 2 *March* 1960)

Abstract—Skarns composed predominantly of Ca pyroxene, Ca amphibole, and biotite occur locally in the Grenville metamorphic terrain of the Canadian pre-Cambrian Shield. The enclosing rocks are Grenville gneisses and limestones, gabbroic rocks, veined gneisses, and granitic rocks. The metamorphic grade of the skarns is identical to that of the enclosing rocks, namely the upper region of the amphibolite facies.

Twelve skarn specimens were selected for chemical study. An investigation is made of the concentrations of Al, Fe, Mg, Mn, Ti, Ca, Na, K, Ba, V, Cr, Zr, Y, and Sc in eleven Ca pyroxenes, ten Ca amphiboles, and eleven biotites.

Consideration is given to the distribution of elements among coexisting minerals. Regular relationships appear when (1) the concentration of an element in a mineral is related to the concentration of the element in a coexisting mineral by a linear or non-linear function, and (2) the linear or non-linear function is itself a function of the concentration of another element in one or both of the coexisting minerals. These relationships indicate that, for the most part, minerals within each skarn specimen closely approached a state of chemical equilibrium.

A preliminary attempt is made to explain the distribution relationships in terms of crystal chemistry.

INTRODUCTION

THE skarns of the present study were encountered between 1955 and 1957, while the writer was examining the geology within an area of the Grenville province. The skarns are principally composed of Ca pyroxene, with smaller proportions of Ca amphibole, biotite, scapolite and calcite. Minerals which appear less commonly are quartz, K feldspar, apatite, sphene, spinel, pyrite, allanite, fluorite, molybdenite, and U-Th minerals. All of the mineral assemblages shall be referred to as "skarn", and the term shall be used without genetic implications.

The major part of the study is a consideration of the distribution of Fe, Mn, Ti, Al, Na, K, Ba, V, Zr, Y, and Sc among coexisting Ca pyroxene, Ca amphibole, and biotite. Distribution coefficients for some elements have been established within the concentration range encountered, and are expressed graphically. We shall be concerned particularly with the regularity of the distributions, and the dependence of the distribution coefficient of one element on variable concentrations of another element. Relationships of this kind give us an indication of chemical communication among the minerals, and of the attainment of chemical equilibrium during the crystallization of the skarns.

Since distribution coefficients are in general a function of temperature, it is important to consider if all of the skarns have crystallized at the same temperature. For this reason we begin the study by briefly considering the metamorphic grade of the skarns, as indicated by the mineral assemblages, and by briefly describing the relationship of the skarns to the enclosing and surrounding gneisses, limestones and other crystalline rocks.

OCCURRENCE

Fig. 1 is a map of a portion of the area which was investigated; it shows the

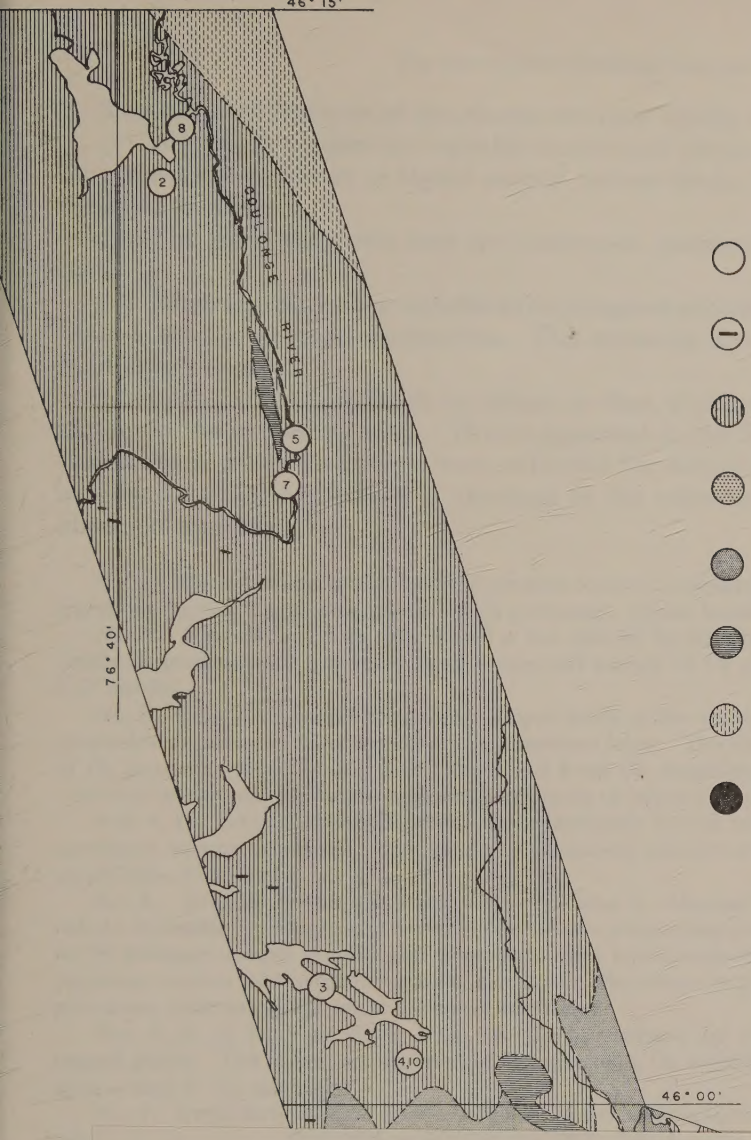
distribution of the principal lithologic units. Numerous small masses of skarn were found within the rocks underlying this area, and the location of ten of these and of twelve specimens which were collected for chemical study is indicated.

The principal lithologic units are Grenville gneisses and limestones, gabbroic rocks (including minor amphibolite and pyroxenite), veined gneisses and, granite rocks. Minerals which compose these units are listed in Table 1. A large number of mineral assemblages and mineral proportions exist, and the rocks are, in general, similar to those encountered in other areas of the Grenville metamorphic terrain.

Table 1. Minerals of principal rock units and skarn

	Grenville gneisses	Gabbroic rocks	Veined gneiss	Granitic rocks	Grenville limestone	Skarn
sillimanite	×	—	×	—	—	—
garnet	×	×	×	×	—	—
biotite	×	×	×	×	×	×
Ca amphibole	×	×	×	×	×	×
anthophyllite	—	×	—	—	—	—
Ca pyroxene	×	×	—	×	×	×
hypersthene	×	×	—	—	—	—
olivine	—	—	—	—	×	—
cordierite	×	×	—	—	—	—
chondrodite	—	—	—	—	×	—
muscovite	×	—	×	×	—	—
K feldspar	×	—	×	×	—	×
plagioclase	×	×	×	×	—	—
scapolite	×	×	—	×	—	×
quartz	×	—	×	×	×	×
magnetite	×	×	×	×	—	—
ilmenite	×	×	×	×	—	—
apatite	×	×	×	×	×	×
zircon	×	×	×	×	—	—
sphene	×	×	×	×	—	×
spinel	×	—	—	—	—	×
pyrite	×	×	×	×	×	×
pyrrhotite	×	—	×	—	×	—
graphite	×	—	—	—	×	—
allanite	×	—	×	×	—	×
tourmaline	—	—	—	×	×	—
calcite	×	×	×	×	×	×
dolomite	—	—	—	—	×	—
fluorite	—	—	—	×	—	×
U-Th minerals	—	—	—	—	—	×
molybdenite	—	—	—	—	—	×
rutile	×	—	×	×	—	—
white mica	×	×	×	×	—	—
ephidote	×	—	×	×	—	—
chlorite	×	×	×	×	—	—
serpentine	—	—	—	—	×	—

× present.
— absent.



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- VEINED GNEISS (BIOTITE- K FELDSPAR GNESSES)
- AMPHIBOLITE - GABBRO - PYROXENITE
- GRENVILLE GNEISSES
- GRENVILLE LIMESTONE

distribution of the principal lithologic units. Numerous small masses of skarn were found within the rocks underlying this area, and the location of ten of these and of twelve specimens which were collected for chemical study is indicated.

The principal lithologic units are Grenville gneisses and limestones, gabbroic rocks (including minor amphibolite and pyroxenite), veined gneisses and, granite rocks. Minerals which compose these units are listed in Table 1. A large number of mineral assemblages and mineral proportions exist, and the rocks are, in general, similar to those encountered in other areas of the Grenville metamorphic terrain.

Table 1. Minerals of principal rock units and skarn

	Grenville gneisses	Gabbroic rocks	Veined gneiss	Granitic rocks	Grenville limestone	Skarn
sillimanite	×	—	×	—	—	—
garnet	×	×	×	×	—	—
biotite	×	×	×	×	×	×
Ca amphibole	×	×	×	×	×	×
anthophyllite	—	×	—	—	—	—
Ca pyroxene	×	×	—	×	×	×
hypersthene	×	×	—	—	—	—
olivine	—	—	—	—	×	—
cordierite	×	×	—	—	—	—
chondrodite	—	—	—	—	×	—
muscovite	×	—	×	×	—	—
K feldspar	×	—	×	×	—	×
plagioclase	×	×	×	×	—	—
scapolite	×	×	—	×	—	×
quartz	×	—	×	×	×	×
magnetite	×	×	×	×	—	—
ilmenite	×	×	×	×	—	—
apatite	×	×	×	×	×	×
zircon	×	×	×	×	—	—
sphene	×	×	×	×	—	×
spinel	×	—	—	—	—	×
pyrite	×	×	×	×	×	×
pyrrhotite	×	—	×	—	×	—
graphite	×	—	—	—	×	—
allanite	×	—	×	×	—	×
tourmaline	—	—	—	×	×	—
calcite	×	×	×	×	×	×
dolomite	—	—	—	—	×	—
fluorite	—	—	—	×	—	×
U-Th minerals	—	—	—	—	—	×
molybdenite	—	—	—	—	—	×
rutile	×	—	×	×	—	—
white mica	×	×	×	×	—	—
ephidote	×	—	×	×	—	—
chlorite	×	×	×	×	—	—
serpentine	—	—	—	—	×	—

× present.
— absent.

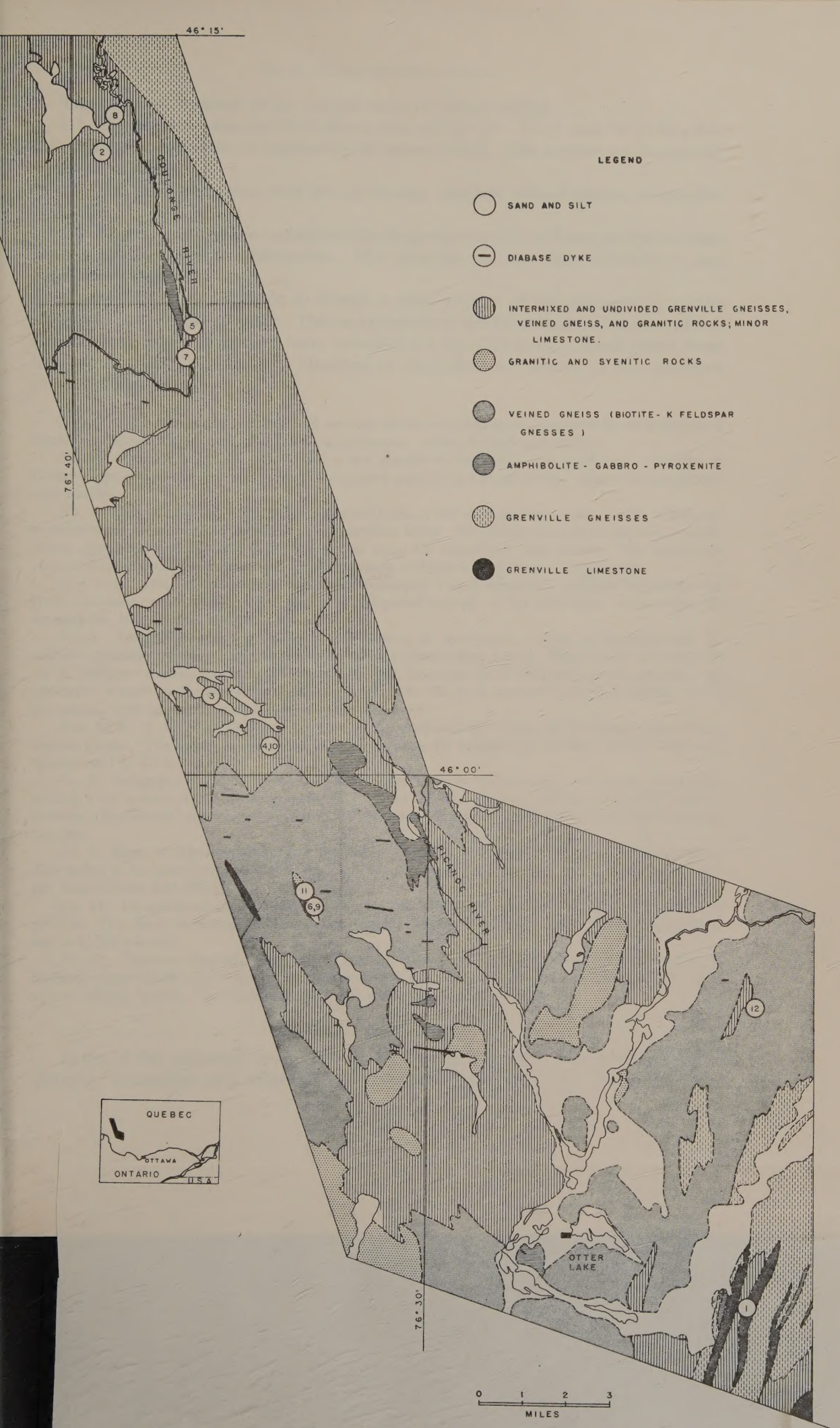


Fig. 1. Simplified geological map of a portion of south-western Quebec, showing the distribution of the principal lithologic units and the position of skarn specimens which were obtained for mineral analysis.

The physical features of the skarns are now briefly noted:

(1) The skarn masses are variable in size and shape. They may be pods a few centimetres in diameter or layers several metres thick. The masses are commonly irregular in shape.

(2) The enclosing rocks may be limestones, gneisses, veined gneiss, or granitic rocks.

(3) Mineral grain size is variable within single skarn units, and may range from less than 1 mm to several centimetres. The minerals are unevenly distributed and randomly oriented.

Commonly it was difficult to obtain a clear picture of the relationship of the skarns to the enclosing rocks. This is apparent in the following description of ten skarns from which specimens were collected for detailed study. Each skarn mass is assigned a number which is identical to the reference number of the specimen obtained therefrom.

No. 1. Mass of unknown shape and several metres in dimension, enclosed by or adjacent a limestone layer. Composed mainly of Ca pyroxene; minor biotite and calcite.

No. 2. Mass of unknown shape and a few metres in dimension enclosed by a mixture of Grenville gneisses and granitic rocks. Composed mainly of Ca pyroxene; minor Ca amphibole and biotite.

No. 3. One of numerous irregularly-shaped pods, a few centimetres in dimension, which are concentrated along certain horizons in a limestone layer. The skarn pods are composed mainly of Ca pyroxene and biotite, with minor and local Ca amphibole and calcite. The limestone contains calcite and dolomite, and small amounts of biotite, serpentine and graphite.

Nos. 4, 10. Irregularly-shaped mass, approximately 1 m in diameter, enclosed by calcite–Ca pyroxene–biotite limestone. The skarn is composed mainly of Ca pyroxene, with minor Ca amphibole, biotite and calcite.

No. 5. Irregularly-shaped mass, a few metres in dimension, which is accompanied by calcite–dolomite limestone and hornblende-biotite–plagioclase gneiss. These rocks are enclosed by K feldspar–quartz granite and pegmatite, and hornblende–K feldspar–quartz granite. Ca pyroxene occurs at limestone–granite contacts. The skarn is composed predominantly of Ca pyroxene, with minor Ca amphibole and biotite.

Nos. 6, 9. A layer of skarn 3 to 6 m thick, enclosed by biotite–K feldspar–plagioclase–quartz gneiss. The skarn is composed of Ca pyroxene, Ca amphibole, biotite, calcite, scapolite, sphene and U-Th minerals.

No. 7. Irregularly-shaped masses of skarn, a few metres in dimension, which are irregularly mixed with calcite–dolomite limestone, K feldspar–quartz granite, and pyroxene–K feldspar syenite. The skarns are composed mainly of Ca pyroxene, with locally minor Ca amphibole and biotite.

No. 8. Mass of unknown shape and size enclosed by a mixture of rock types, mainly granitic. The skarn is an assemblage of 1 mm grains of Ca pyroxene and Ca amphibole, with less than 1 per cent biotite and calcite.

No. 11. Lens-shaped mass of skarn, a few metres in dimension, enclosed by a heterogeneous granite. The skarn is composed of calcite, Ca pyroxene, Ca amphibole, biotite, scapolite, apatite and a U-Th mineral.

No. 12. Tabular-shaped mass, a few metres thick, overlain and underlain by biotite–K feldspar–plagioclase-quartz gneiss (veined gneiss). The skarn is composed of Ca pyroxene, with minor calcite, biotite, Ca amphibole, sphene, quartz and molybdenite.

Mineral Assemblages

Some of the principal rock units (Table 1) contain small amounts of epidote, chlorite, muscovite and serpentine, minerals representative of the greenschist,

epidote amphibolite, or lower part of the amphibolite facies. Almost invariably it can be shown that these minerals are the products of a retrograde recrystallization. Rocks containing hypersthene, a mineral representative of the granulite facies, are rare. Thus the mineral assemblages of the principal rock units are correlated with the upper region of the amphibolite facies, as defined by Eskola (1939), and later by Turner (1948) and Ramberg (1952a). There is no evidence of a significant change of metamorphic grade across the area. These conclusions were stated previously by the writer Kretz (1959) in connexion with a detailed study of the Grenville gneisses from the same area.

Minerals that have been observed in the skarns are listed in Table 1. The mineral assemblages of twelve skarn specimens which were selected for chemical study are listed in Table 2.

Table 2. Mineral assemblages of twelve skarn specimens which were selected for mineral analysis

Specimen no.	Reference no.	Ca pyroxene	Ca amphibole	Biotite	Scapolite	Calcite	Fluorite	Apatite
324A-55	1	○	—	○	—	×	—	—
N46-57	2	○	○	○	—	—	—	—
70-57	3	×	○	○	—	×	—	—
235-57	4	○	○	○	—	×	—	—
211-57	5	○	×	○	—	—	—	—
Yates-55	6	○	○	○	—	×	×	×
212-57	7	○	—	○	—	—	—	—
184-57	8	○	○	×	—	×	—	—
Yates 2-55	9	○	○	○	—	×	—	—
234-57	10	—	○	○	×	×	—	—
117-56	11	○	○	○	—	×	—	—
440A-55	12	○	○	○	—	×	—	—

○ Mineral analyzed.
× Mineral present but not analyzed.
— Mineral absent.

The common skarn assemblage pyroxene–amphibole–biotite* occurs also in many limestones and gneisses of the area. This assemblage is stable in the entire range of the amphibolite facies (Ramberg 1952; Fyfe *et al.*, 1958). The fact that epidote has not been found in any of the skarns suggests that the rocks crystallized beyond the stability field of this mineral, i.e. within the upper region of the amphibolite facies. The coexistence of calcite and quartz in some skarns and the complete absence of wollastonite indicates that relatively-high temperature conditions (possibly correlative with the granulite facies) were not attained. According to Ramberg (1952), scapolite, sphene and apatite are stable in the upper region of the amphibolite facies. This is confirmed by the occasional presence of these minerals in the Grenville gneisses which were previously assigned

* In subsequent discussions, Ca pyroxene and Ca amphibole will be referred to as pyroxene and amphibole.

to this facies. Very little is known about the stability fields of other skarn minerals such as allanite, fluorite and molybdenite.

The above discussion leads to the conclusion that the skarns crystallized within the pressure–temperature field represented by the upper region of the amphibolite facies. This is the same metamorphic grade as that of the enclosing Grenville gneisses, limestones and other rocks. Many skarns occur as inclusions in limestone or gneiss, or as layers within gneiss, and are not at all situated near rocks which are supposed to have crystallized at magmatic temperatures. These data indicate that the skarns are the products of regional metamorphism and have all crystallized at the same or nearly the same temperature. This finding is relevant to the following consideration of the distribution of elements among the skarn minerals.

The Chemical Composition of Pyroxene, Amphibole, and Biotite

The mineral analyses are listed in Table 3, which includes two analyses (one pyroxene and one amphibole) from a Grenville gneiss. The gneiss is composed of pyroxene, amphibole, plagioclase, apatite and ilmenite.

Before evaluating the mineral composition data, the mineral separation and analytical techniques are briefly described.

Mineral separation

The selected rock specimens were about 4 or 5 cm in diameter, and the minerals in each specimen are considered to be a coexisting assemblage. Minerals were concentrated by use of an isodynamic separator, by sliding grains on a sheet of paper, and by hand sorting. All pyroxene and amphibole grains were broken to about 0·5 mm and biotite grains to about 1·0 mm. The mineral concentrates were finally purified by examining each grain and removing foreign or composite grains with a needle.

On the basis of microscopic examinations, the purity of the mineral concentrates was greater than 99 per cent by volume.

Analytical procedure

The concentrations of Si, Al, total Fe, Mg, Mn, Ti, Ca, Ba, V, Cr, Zr, Y and Sc in pyroxene, amphibole and biotite were investigated spectrographically. A Beckman flame photometer was used to determine Na and K concentrations.

The spectrographic procedure was developed by Joensuu, and is similar to that described by Goldsmith *et al.* (1955.) Working curves were obtained from chemically-analysed minerals and from mixtures prepared by Joensuu. Synthetic mixtures were used as standards for the flame photometric analyses.

The precision is as follows: SiO_2, ± 10 per cent; Al_2O_3, ± 5 per cent; Fe, ± 2 per cent; MgO, ± 10 per cent; MnO, ± 5 per cent; TiO_2, ± 10 per cent for low concentrations, ± 20 per cent for higher concentrations; CaO ± 10 per cent; BaO, ± 10 per cent; V_2O_3, ± 10 per cent; Cr_2O_3, ± 10 per cent; ZrO_2, ± 20 per cent; Y_2O_3, ± 10 per cent; Sc_2O_3, ± 10 per cent; K_2O, ± 2 per cent; Na_2O, ± 5 per cent. The values are listed as weight per cent of the amount present.

Table 3. Mineral compositions

	Ref. no. of rock	1	2	4	5	6	7	8	9	11	12	G
		Ca pyroxene										
Oxide (Wt. %)	Al_2O_3	1·7	0·95	2·3	1·1	2·1	1·7	3·3	0·33	1·7	1·1	2·2
	Fe°	0·50	0·88	0·91	1·0	2·2	2·5	3·3	0·37	1·16	4·4	6·5
	Fe° = FeO	0·64	1·13	1·17	1·3	2·8	3·2	4·2	0·48	1·49	5·65	8·35
	MgO	17·6	17·6	17·6	17·6	16·5	17·2	16·0	17·3	16·0	13·8	11·6
	MnO	0·039	0·065	0·074	0·074	0·135	0·083	0·14	0·035	0·094	0·15	0·32
	TiO_2	0·099	0·055	0·033	0·081	0·040	0·125	0·028	0·013	0·087	0·056	0·142
	Na_2O	0·44	0·23	0·41	0·33	0·37	0·35	0·55	0·16	0·37	0·45	0·6
	K_2O	0·50	0·10	<0·10	0·10	<0·10	<0·10	0·10	0·10	0·10	0·10	<0·10
	BaO	0·040	0·014	<0·01	0·021	<0·01	<0·01	<0·01	<0·01	—	<0·01	<0·01
	V_2O_3	—	—	—	—	—	0·012	0·016	—	—	—	0·056
	Cr_2O_3	—	—	—	—	—	—	—	—	—	—	0·027
	ZrO_2	—	—	—	—	—	—	0·016	—	—	—	—
	Y_2O_3	—	—	—	—	—	—	—	—	—	—	—
	Sc_2O_3	—	—	—	—	—	—	~0·005	—	—	—	0·013
$\frac{\text{(Element Wt. \%)}}{\text{(Atomic Wt.)}} \times 100$	Al	3·34	1·86	4·52	2·16	4·12	3·34	6·48	0·65	3·34	2·16	4·32
	Fe	0·89	1·57	1·63	1·81	3·9	4·45	5·85	0·668	2·08	7·86	11·6
	Mg	43·6	43·6	43·6	43·6	40·9	42·6	39·7	42·8	39·7	34·2	28·8
	Mn	0·055	0·092	0·104	0·1043	0·19	0·117	0·198	0·0494	0·132	0·212	0·452
	Ti	0·124	0·069	0·0413	0·101	0·05	0·157	0·035	0·0163	0·109	0·0701	0·178
	Na	1·42	0·74	1·32	1·07	1·20	1·13	1·78	0·517	1·20	1·45	1·97
	K	1·06	0·21	<0·21	0·21	<0·21	<0·21	0·21	0·21	0·21	0·21	<0·21
	Ba	0·026	0·0091	<0·006	0·014	<0·006	0·006	<0·006	<0·006	—	<0·006	<0·006
Atomic ratio	Fe/Σ	0·0199	0·0346	0·036	0·0398	0·0866	0·094	0·128	0·0154	0·0495	0·186	0·282
	Mg/Σ	0·975	0·961	0·96	0·957	0·91	0·90	0·867	0·985	0·945	0·807	0·702
	Mn/Σ	0·00123	0·00203	0·0023	0·00228	0·0042	0·00248	0·0043	0·00114	0·00314	0·005	0·011
	Ti/Σ	0·00278	0·00152	0·00091	0·00222	0·00111	0·00332	0·00076	0·000374	0·0026	0·00165	0·00434

Footnotes on p. 168.

Table 3—(*continued*)—Mineral compositions

	Ref. no. of rock	2	3	4	6	8	9	10	11	12	G
	Ca Amphibole										
(Oxide Wt. %)	Al_2O_3	2·0	14·5	15·0	14·5	14·5	0·64	14·0	13·0	3·2	10·0
	Fe°	1·5	0·77	2·2	4·1	6·8	0·78	2·05	2·28	5·6	10·9
	Fe° = FeO	1·9	0·99	2·8	5·3	8·7	1·0	2·64	2·93	7·2	14·0
	MgO	22·5	19·5	20·0	18·5	14·4	20·6	17·5	17·1	16·0	12·3
	MnO	0·076	0·047	0·080	0·118	0·133	0·050	0·035	0·076	0·123	0·240
	TiO_2	0·078	0·165	0·18	0·14	1·15	0·030	0·095	0·29	0·20	1·56
	Na_2O	0·60	4·8	2·65	2·32	2·17	0·70	2·47	2·35	0·50	1·65
	K_2O	0·30	1·50	1·40	1·55	1·60	0·24	1·4	1·55	0·35	1·00
	BaO	0·011	0·016	0·033	0·028	0·037	<0·01	0·040	<0·01	<0·01	0·016
	V_2O_3	—	0·012	—	0·012	0·037	—	—	0·016	0·021	0·124
	Cr_2O_3	—	—	—	—	—	—	—	—	—	0·067
	Zr_2O_3	—	—	—	—	0·020	—	—	—	—	<0·015
	Y_2O_3	—	—	0·007	0·0085	<0·005	—	—	0·015	—	—
	Sc_2O_3	—	—	—	—	0·008	—	—	—	—	0·016
$\frac{\text{(Element Wt. \%)}}{\text{Atomic Wt.}} \times 100$	Al	3·93	28·5	29·5	28·5	28·5	1·26	27·5	25·6	6·3	19·6
	Fe	2·64	1·38	3·9	7·38	12·1	1·39	3·67	4·07	10·0	19·5
	Mg	55·7	48·3	49·6	45·8	35·7	51·0	43·3	42·4	39·7	30·5
	Mn	0·107	0·066	0·113	0·166	0·188	0 0705	0 0494	0·107	0·174	0·339
	Ti	0·098	0·206	0·225	0·175	1·44	0·0376	0·120	0·363	0·25	1·95
	Na	1·94	15·5	8·57	7·5	7·0	2·26	7·98	7·60	1·61	5·33
	K	0·636	3·18	2·97	3·29	3·4	0·509	2·97	3·29	0·742	2·12
	Ba	0·0072	0·0104	0·0215	0·0183	0·0242	<0·006	0·0261	<0·006	<0.006	0·0104
Atomic ratio	Fe/Σ	0·0452	0·0276	0·0725	0·138	0·244	0·0265	0·0779	0·0867	0·20	0·373
	Mg/Σ	0·952	0·967	0·92	0·857	0·722	0·972	0·92	0·903	0·793	0·583
	Mn/Σ	0·00183	0·00132	0·0021	0·0031	0·0038	0·00134	0·00105	0·00228	0·00348	0·00648
	Ti/Σ	0·00168	0·00412	0·00417	0·00327	0·029	0·000716	0·00255	0·00774	0·005	0·0372

Table 3—(*continued*)—Mineral compositions

	Ref. no. of rock	1	2	3	4	5	6	7	9	10	11	12
		Biotite										
Oxide (Wt. %)	Al_2O_3	13·0	14·5	15·6	13·0	15·0	12·3	16·0	9·8	12·8	13·0	13·0
	Fe°	0·53	1·8	0·57	1·35	2·1	2·1	4·9	0·75	1·13	1·0	9·6
	Fe° = FeO	0·68	2·3	0·73	1·7	2·7	2·7	6·3	0·96	1·45	1·28	12·3
	MgO	23·5	26·0	25·0	25·5	25·5	25·0	22·5	25·0	24·0	24·0	16·4
	MnO	0·015	0·033	0·016	0·031	0·034	0·053	0·041	0·0135	0·030	0·035	0·049
	TiO_2	1·90	0·70	0·28	0·21	0·82	0·167	1·75	0·063	0·14	0·19	2·5
	CaO	0·36	0·13	0·36	0·16	0·16	0·21	0·20	0·32	0·31	0·21	0·27
	Na_2O	0·30	0·25	0·75	0·52	0·24	0·50	0·21	0·50	0·50	0·54	0·15
	K_2O	9·7	9·9	9·0	9·6	9·7	9·5	9·6	9·2	9·0	9·2	9·1
	BaO	>0·50	>0·50	>0·50	>0·50	>0·50	>0·50	>0·50	0·18	>0·50	>0·50	>0·50
	V_2O_3	—	—	—	—	0·011	—	0·020	—	—	—	0·035
	Cr_2O_3	—	—	—	—	—	—	—	—	—	—	—
	ZrO_2	—	—	0·016	—	—	—	—	—	—	—	—
	Y_2O_3	—	—	—	—	—	—	—	—	—	—	—
	Sc_2O_3	—	—	—	—	—	—	—	—	—	—	—
$\frac{\text{(Element Wt. \%)}}{\text{(Atomic Wt.)}} \times 100$	Al	25·5	28·4	30·6	25·5	29·4	24·2	31·4	19·2	25·1	25·5	25·5
	Fe	0·95	3·2	1·02	2·37	3·76	3·76	8·77	1·34	2·02	1·78	17·1
	Mg	58·2	64·5	62·0	63·2	63·2	62·	55·7	62·0	59·5	59·5	40·7
	Mn	0·0212	0·0465	0·0226	0·044	0·048	0·0747	0·0578	0·019	0·0423	0·0494	0·0692
	Ti	2·38	0·878	0·35	0·263	1·025	0·209	2·19	0·0789	0·175	0·238	3·13
	Ca	0·64	0·232	0·64	0·285	0·285	0·374	0·356	0·57	0·552	0·374	0·48
	Na	0·969	0·807	2·42	1·68	0·775	1·61	0·678	1·61	1·61	1·74	0·484
	K	20·6	21·0	19·1	20·4	20·6	20·15	20·4	19·5	19·1	19·5	19·3
	Ba	>0·33	>0·33	>0·33	>0·33	>0·33	>0·33	>0·33	0·117	>0·33	>0·33	>0·33
Atomic ratio	Fe/Σ	0·0154	0·0467	0·0161	0·036	0·0553	0·057	0·132	0·0212	0·0327	0·0289	0·280
	Mg/Σ	0·945	0·94	0·978	0·96	0·930	0·94	0·834	0·98	0·964	0·967	0·667
	Mn/Σ	0·000344	0·00068	0·000356	0·00067	0·000706	0·00113	0·000867	0·0003	0·000686	0·000802	00·0113
	Ti/Σ	0·0386	0·0128	0·0055	0·004	0·0151	0·00316	0·0329	0·00124	0·00284	0·0038	0·0513

∼ Approximately.
> Greater than.
< Less than.
— Below the limit of detection,
i.e. less than about 0·005 weight per cent.
Σ Fe + Mg + Mn + Ti.

The probable error, resulting from lack of precision was reduced by analysing each mineral three times.

Ca *pyroxene*. The SiO_2 and CaO concentrations of all pyroxenes were determined by the spectrographic method to be approximately 50 per cent and 22 per cent, respectively. The figures are not listed because of their inaccuracy. These values, together with the listed MgO concentrations indicate that the pyroxene compositions closely approach that of diopside, $Ca(Mg, Fe)Si_2O_6$. The 6-co-ordinated occupants are considered to be Mg, Fe, Mn, Ti, and unknown amounts of Al. Atomic ratios have been calculated on the basis of (Mg + Fe + Mn + Ti) = 1·0, and are listed in Table 3.

Ca *amphibole*. SiO_2 and CaO concentrations of all amphiboles were found to range from 38 to 50 per cent and 9 to 13 per cent, respectively. This confirms that the minerals are Ca amphiboles of approximate formula

$$Ca_2(Mg, Fe, Al)_5(Al, Si)_8O_{22}(OH)_2.$$

The Al_2O_3 content of the analysed amphiboles ranges from 0·64 to 15 weight per cent, but the available data do not permit a calculation of the proportion of Al in 6- and 4-co-ordinated positions. Ti and Mn atoms are considered to occupy 6-co-ordinated positions, together with Mg and Fe, and the atomic ratios of these elements are calculated on the basis of (Mg + Fe + Mn + Ti) = 1·0. The values are listed in Table 3.

Biotite. The SiO_2 concentration of the biotites was found to range from 37 to 41 per cent. The approximate formula of these minerals is

$$K_1(Mg, Fe, Al)_3(Al_1Si_3)O_{10}(OH)_2.$$

In the skarn biotites the ratio (K, Ca, Na, Ba) : (Mg, Fe, Mn, Ti) is very nearly 1 : 3, which indicates that nearly all of the Al atoms occupy 4-co-ordinated positions. As with pyroxene and amphibole, the 6-co-ordinated positions are considered to be occupied by Mg, Fe, Mn and Ti, and the atomic ratios have been calculated on the basis of (Mg + Fe + Mn + Ti) = 1·0. The values are listed in Table 3.

Distribution of Elements among Coexisting Pyroxene, Amphibole, and Pyroxene

Previous study

The distribution of Fe and Mg between coexisting olivine and orthopyroxene was investigated by Ramberg and DeVore (1951). An expression of the distribution coefficient was developed, and the pressure dependence and temperature dependence of the coefficient were evaluated. Bethke *et al.* (1958) have established the pressure dependence of a distribution coefficient by experimental work in a sulphide system, and have shown that both phases of the system are apparently ideal mixtures. The writer (Kretz, 1959) established distribution coefficients for certain elements and phases in naturally-occurring silicate systems, and presented the coefficients in graphical form by use of a Roozeboom diagram. The graphical method is particularly helpful in detecting variations of a distribution coefficient which are produced by variations in the concentration of another element. The use of this method is continued in the present study.

The application of crystal chemistry to the distribution of elements among coexisting minerals has been considered in detail, especially by RAMBERG (1952b) and DEVORE (1955a, b, 1957). The principles developed by these writers will be briefly considered in the present study.

Theoretical considerations

Consider a chemical system at a temperature T' and pressure P' with two or more phases present at equilibrium. Two of the phases, α and β have the formula (A, B)Y_m and (A, B)Z_n, respectively, where A, B, Y and Z are chemical species. The compositions of the phases are indicated by the atomic or molecular ratios X_A^{α} and X_A^{β}, respectively. $X_A = A/(A + B)$. We now wish to obtain a relationship between X_A^{α} and X_A^{β} for all possible values of X_A.

RAMBERG and DEVORE (1951) considered a problem of this type and developed the equation:

$$\frac{X_A^{\alpha}}{1 - X_A^{\alpha}} \cdot \frac{1 - X_A^{\beta}}{X_A^{\beta}} = \exp\left[\Delta F/(RT)\right] \tag{1}$$

The left-hand side of this equation is referred to as the distribution coefficient. ΔF is an energy term which is characteristic of the phases α and β, R is the gas constant, and T is the absolute temperature. The equation applies only in the case that α and β are ideal mixtures. At a specified T and P the right-hand side of the equation is a constant, and X_A^{α} plotted against X_A^{β} for different values of X_A produces a characteristic curve, as previously described by the writer (KRETZ, 1959).

It can be shown that when α and β are not ideal mixtures, i.e. for the general case, the following equation applies (YUTZY and KOLTHOFF, 1937).

$$\frac{X_A^{\alpha}}{1 - X_A^{\alpha}} \cdot \frac{1 - X_A^{\beta}}{X_A^{\beta}} = K_f \exp\left[\Delta F/(RT)\right] \tag{2}$$

K_f is a value determined by the activity coefficients of AY_m, BY_m, AZ_n, and BZ_n in α and β. It is a function of X_A^{α} and X_B^{β} and consequently the distribution coefficient is not a constant. In this case, X_A^{α} plotted against X_A^{β} produces an irregular curve.

When one of the chemical species, for example A, is present in small amounts in both phases, K_f is a constant value regardless if α and β are ideal mixtures or not. Then:

$$\frac{X_A^{\alpha}}{1 - X_A^{\alpha}} \cdot \frac{1 - X_A^{\beta}}{X_A^{\beta}} \simeq \frac{X_A^{\alpha}}{X_A^{\beta}} = \text{constant} \tag{3}$$

which is the familiar Nernst's distribution equation.

We shall now consider two phases α and β, with formulae (A, B, C)Y_m and (A, B, C)Z_n, respectively. When α and β are ideal mixtures with reference to A, B, and C it can be shown that equation (1) remains valid.* Now $X_A = A/(A + B + C)$, and the distribution coefficient of A may be dependent on the B : C ratio in either phase. When α and β are not ideal mixtures, i.e. for the general

* This and other theoretical considerations will be discussed in greater detail in a separate paper.

case, equation (2) is valid. Now K_f is a function not only of X_A^{α} and X_A^{β} but also of X_C^{α} and X_C^{β}, and the distribution curve obtained by plotting X_A^{α} against X_A^{β} will shift as a function of the B : C ratio in either phase, regardless if the phases are ideal or not.

The temperature dependence and pressure dependence of the distribution coefficient have been evaluated by Ramberg and DeVore. With reference to the distribution of Fe and Mg between olivine and orthopyroxene, the pressure dependence was calculated to be negligible within the range of pressure which may be expected within the earth's crust. The temperature dependence is significant, and in the event that both phases are ideal mixtures it may be calculated, provided that appropriate entropy data are available. With reference to the minerals of the present study, the data are not available and a theoretical evaluation of the temperature dependence is not possible.

In view of the above considerations, we shall proceed with the study of the skarn minerals as follows. We are concerned mainly with the 6-co-ordinated occupants of pyroxene, amphibole and biotite; these are considered to be Mg, Fe, Mn, Ti and Al. Ideally, the atomic ratio of one element, for example Mn, should be calculated as: number of Mn atoms/total number of 6-co-ordinated atoms. The charge and size of the 6-co-ordinated occupants is so variable that we must expect large deviations from ideal mixing; they may be so large that the structural sites occupied by Al, for example, are not available to the other atoms. For this reason it may be permissible to neglect Al in the atomic ratio calculations. This procedure will be followed, mainly because the exact number of Al atoms in the 6-co-ordinated positions is not known, and the atomic ratio of Mn, for example is calculated as Mn/(Mg + Fe + Mn + Ti).

Because the charge of a crystal must remain neutral, we may expect large deviations from ideal mixing with reference to ions which occupy structural sites that are occupied mostly by ions of a different charge number. For example, we may anticipate that variations of Na : Ca in 8-co-ordinated positions of pyroxene will influence the Ti distribution coefficient in pyroxene–biotite, or that variations of Ti content in 6-co-ordinated positions of pyroxene will influence the Na distribution coefficient in pyroxene–biotite. It is also reasonable to expect that even an ideal mixing of an element in the 6-co-ordinated positions of pyroxene may be affected by changes in the Na : Ca ratio within the 8-co-ordinated positions of the same crystal.

To demonstrate the procedure that will be employed, we choose an example, namely the distribution of the element A between pyroxene and biotite. First, an attempt is made to find a relationship between $X_A^{\text{pyrox.}}$ and $X_A^{\text{bi.}}$ as expressed by equation (1) or (2). This is done by plotting $X_A^{\text{pyrox.}}$ against $X_A^{\text{bi.}}$ for different mineral pairs. If the points define a smooth curve we conclude that equilibrium was attained and that the effect of the numerous compositional variables has not been great enough to alter the distribution coefficient noticeably. If the points produced by the plot are scattered we expect that the distribution coefficient has been displaced by the variable concentration of another element in one or both minerals. If a relationship of this type is found, it is shown by plotting the distribution coefficient against the concentration of the other element in one of the two

minerals. We conclude again that equilibrium was attained and that the effect of other variables is negligibly small. If no relationship between $X_A^{pyrox.}$ and $X_A^{bi.}$ can be found, we conclude that one or more of the following possibilities is responsible.

(1) The distribution coefficient is a function of the concentration of an element which has not been considered in the mineral analysis, and therefore the relationship can not be detected.

(2) The distribution coefficient is a function of several compositional variables, and the relationships are therefore too complex to be detected.

(3) Inclusions of one or more sub-microscopic phases exist in the minerals and have contaminated the analyses.

(4) Variations in the temperature of equilibration or quenching within the group of mineral pairs have resulted in corresponding variations in the distribution coefficient.

(5) A condition of chemical equilibrium with reference to the particular component and phases was not established in all skarn specimens, or it was not retained. In this connexion it is important to consider the size of natural chemical systems (thermodynamic systems). Spheres of chemical communication may be different in size with reference to different elements, depending on their mobility, and may vary in size as a function of temperature. Unless the volumes of rock chosen for study are relatively small, irregularities in element distributions may appear even though local equilibrium was established.

Distribution of Fe

The $Fe^{2+} : Fe^{3+}$ ratios were not determined and the present discussion deals with the distribution of total Fe among the minerals.

Pyroxene–amphibole (*Fig.* 2). The distribution of Fe between pyroxene and amphibole is shown in Fig. 2. Each point on the diagram is a plot of the atomic ratio of Fe in amphibole against this ratio in coexisting pyroxene. The numbers adjacent the points are the reference numbers of the rocks from which the mineral pairs were taken (Table 2).

The distribution points are somewhat scattered. We note, however, that a straight line can be drawn through points 9, 2 and 12 (line *A*). The amphiboles of these mineral pairs contain relatively-low concentrations of Al, Na and K, as indicated by the table which accompanies Fig. 2. Another line can be drawn to pass near points 4, 11, 6 and 8 (line *C*). The amphiboles of these mineral pairs contain relatively high concentrations of Al, Na and K. The distribution point *G*, which refers to minerals from a pyroxene–amphibole gneiss, falls so that a line through the point may lie between lines *A* and *C*. The amphibole of this mineral pair contains intermediate concentrations of Al, Na and K.

It is apparent that the position of the distribution curve is dependent on the Al, Na or K content of the amphiboles. Because the variation of Al content is much greater than that of Na and K the Fe distribution coefficient is considered to be dependent mainly on the Al content rather than the Na or K content of the amphiboles. If this correlation is valid, an increase in the Al concentration of amphibole causes this mineral to acquire a higher concentration of Fe relative to that of the coexisting pyroxene, i.e. the distribution curve in Fig. 2 shifts to the left.

It is puzzling why distribution curves *A* and *C* do not intersect the origin. A possible cause of this may lie in the fact that the diagram shows the distribution of $Fe^{2+} + Fe^{3+}$ between the minerals. If Fe^{3+} is confined mainly to amphibole, we may expect the distribution curves to bend rather sharply and proceed towards the origin.

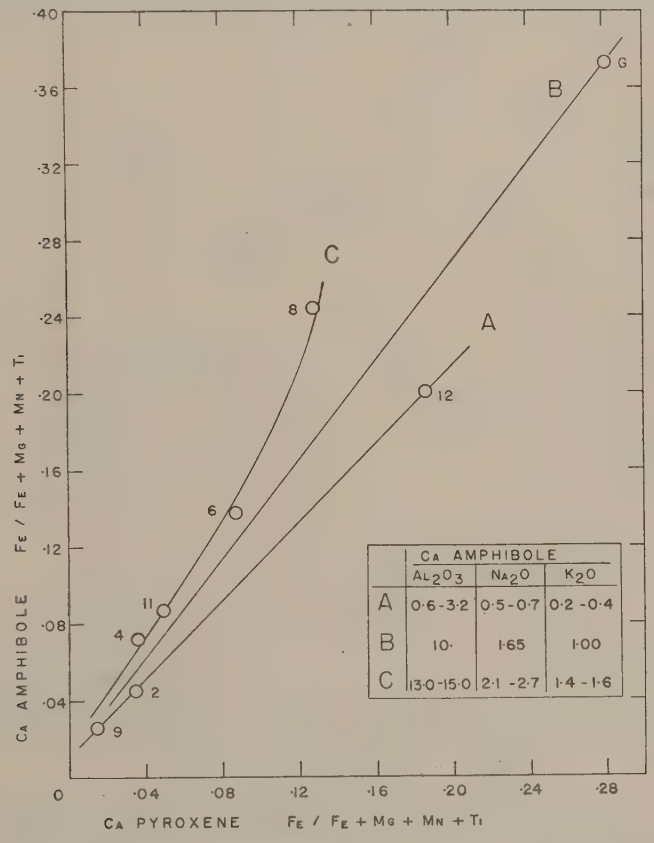


Fig. 2. Distribution of iron between pyroxene and amphibole.

Within the composition range of the pyroxene–amphibole pairs, and at values of X_{Fe} greater than about 0·02, the distribution of Fe between pyroxene and low-Al amphibole (line *A*) can be expressed by the equation:

$$(X_{Fe}^{amph.} - 0{\cdot}01)/(X_{Fe}^{pyrox.}) = 1{\cdot}0 \qquad (4)$$

The distribution of Fe between pyroxene and Al amphibole (line *C*) is evidently a non-linear relationship, as shown by the curved line in Fig. 2.

Amphibole–biotite (*Fig.* 3). again, distribution points which refer to mineral pairs in which amphiboles contain relatively-low concentrations of Al, Na and K fall on a straight line (line *A*). Distribution points which refer to mineral pairs in which the amphiboles contain relatively-high concentrations of Al, Na and K appear to define a curved line (line *C*).

It is apparent that the position of the distribution curve is dependent on the Al, Na or K content of the amphiboles, and again it is supposed that it is dependent mainly on the Al concentration. An increase of Al in amphibole causes the mineral to acquire a higher concentration of Fe relative to that of the coexisting biotite, i.e. the distribution curve in Fig. 3 shifts to the left.

Line *A*, when projected, does not intersect the origin. A possible cause of this has already been noted.

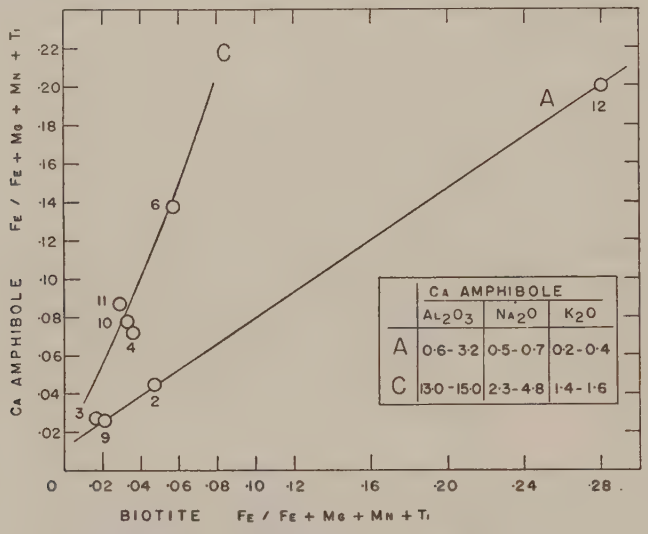


Fig. 3. Distribution of iron between amphibole and biotite.

Within the limited range of Fe concentration and at values of X_{Fe} greater than about 0·02, the distribution of Fe between low-Al amphibole and biotite is expressed by the equation:

$$(X_{Fe}^{amph.} - 0{\cdot}01)/(X_{Fe}^{bi.}) = 0{\cdot}67 \qquad (5)$$

The distribution of Fe between Al amphibole and biotite (line *C*) is not well established but apparently is a non-linear relationship. Because the distribution points are somewhat scattered, this line was located by combining the relationship:

$$X_{Fe}^{pyrox.} = 1{\cdot}5\ X_{Fe}^{bi.} \qquad (6)$$

which was found in specimens (6) and (11), and is shown in Fig. 4, and the $X_{Fe}^{pyrox.} - X_{Fe}^{amph.}$ relationship (line *C*) of Fig. 2.

In a study of the distribution of Fe between Al amphibole and biotite, the writer (Kretz, 1959) found that Fe is approximately equally distributed between these two minerals. It is therefore surprising to find that Al amphiboles in the skarns contain nearly twice as much Fe as the coexisting biotites. In looking for an explanation of this it was found that skarn amphiboles contain more Na than amphiboles from gneisses (2·17 to 4·8 compared with 1·12 to 1·65 per cent Na_2O). Possibly an increase in the Na content of amphibole causes an increase in the $X_{Fe}^{amph.}/X_{Fe}^{bi.}$ ratio. If so, the shift of the distribution curves in Figs. 2 and 3 may be

partly attributed to variations of Na content of the amphiboles. More data are needed to determine the relative influence of variations of Al, Na and K concentrations of amphibole on the affinity of this mineral for Fe.

Pyroxene–biotite (*Fig.* 4). We shall consider first the skarns which contain low-Al amphiboles (specimens 9, 2 and 12). From equations (4) and (5), the calculated relationship between $X_{Fe}^{pyrox.}$ and $X_{Fe}^{bi.}$ is:

$$X_{Fe}^{pyrox.} = 0{\cdot}67\ X_{Fe}^{bi.} \tag{7}$$

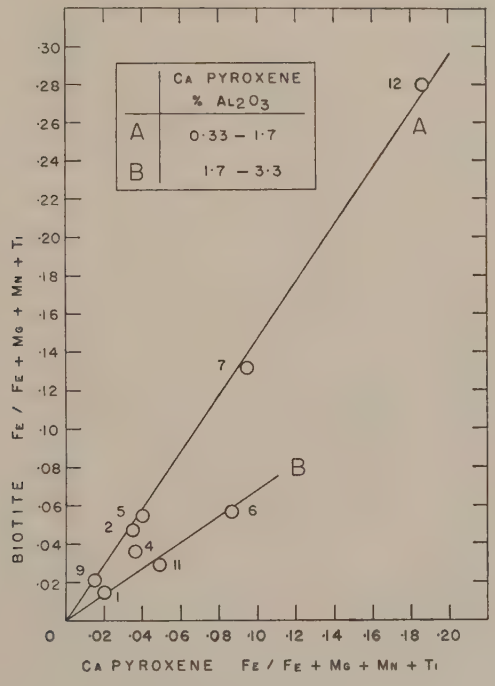


Fig. 4. Distribution of iron between pyroxene and biotite.

which is the equation of line *A*, Fig. 4. Distribution points from two other mineral pairs (from specimens 5 and 7) also fall on this line.

It is not reasonable that the composition of amphibole in a skarn may influence the distribution of Fe between pyroxene and biotite in the same rock. Yet the distribution of Fe between these two minerals appears to be different when Al amphibole is present than when low-Al amphibole is present. This is shown by the position of points (11), (4) and (6) in Fig. 4 relative to the position of points (9), (2) and (12). The explanation of this may be that pyroxenes which coexist with Al amphiboles tend to contain higher Al concentrations (1·7 to 2·3 compared with 0·33 to 1·7 per cent Al_2O_3) than those which coexist with low-Al amphiboles. An increase of Al content of pyroxene may increase the affinity of this mineral for Fe, and cause the distribution curve to shift to the right, as shown in Fig. 4. More information is needed to extend this part of the investigation.

Distribution of Mn

Amphibole–biotite (*Fig.* 5). The diagram includes some distribution points (marked by crosses) which represent the distribution of Mn between amphibole and biotite in Grenville gneisses (Kretz, 1959).

Within the concentration range now considered, the relationship between $X_{Mn}^{amph.}$ and $X_{Mn}^{bi.}$ is linear and can be expressed by the equation:

$$X_{Mn}^{amph.} = 3{\cdot}2\ X_{Mn}^{bi.} \tag{8}$$

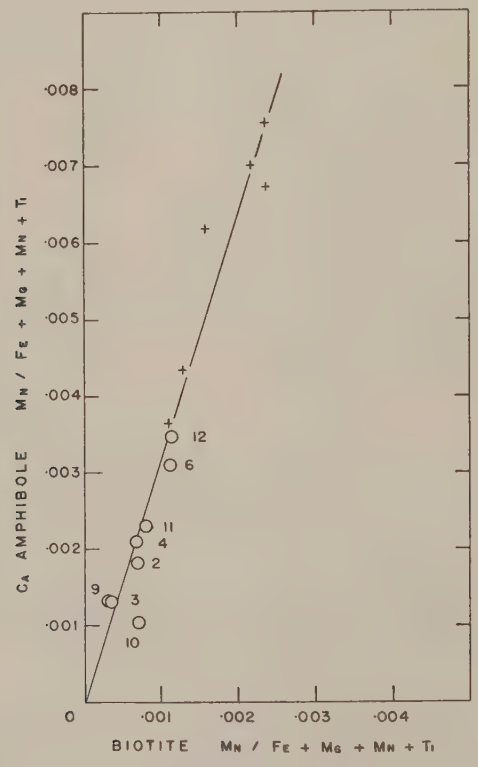


Fig. 5. Distribution of manganese between amphibole and biotite.

The distribution in specimen (10) is the only one that deviates significantly from this relationship.

Pyroxene–biotite (*Fig.* 6). The distribution points fall remarkably close to a line. At low concentrations of Mn the line is straight and intersects the origin, and at higher concentrations it is slightly curved towards the pyroxene axis.

Pyroxene–amphibole (*Fig.* 7). Compared with Fig. 5 and Fig. 6 the distribution points are slightly more scattered. For this reason the curve in Fig. 7 was located independently, on the basis of the $X_{Mn}^{amph.}$–$X_{Mn}^{bi.}$ relationship of Fig. 5 and the $X_{Mn}^{bi}X_{Mn}^{pyrox.}$ relationship of Fig. 6. The Mn distribution between pyroxene and amphibole in specimen (8) and possibly in (1) and (9) deviated somewhat from the regular distribution in the remaining specimens.

It is noteworthy that the distribution of Mn among pyroxene, amphibole and

biotite in the skarns is not affected by the numerous other compositional variables of the minerals, or if an effect is present it is not detectable. The slight deviations of points from the distribution curves could be attributed to analytical error alone. However, the apparently irregular distribution of Mn in amphibole–biotite of specimen (10) and in pyroxene–amphibole of specimen (8) must be accounted for by one of the following causes.

(1) The distributions are affected by compositional changes which are not apparent in the available analytical data.

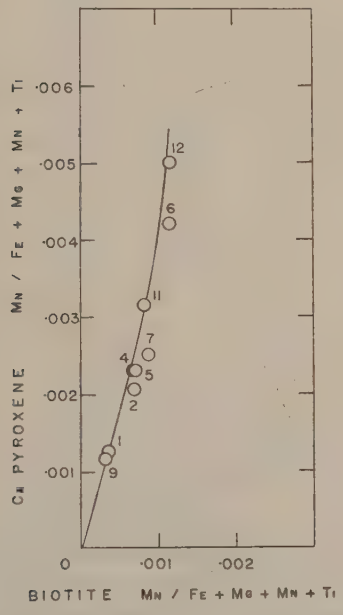


Fig. 6. Distribution of manganese between pyroxene and biotite.

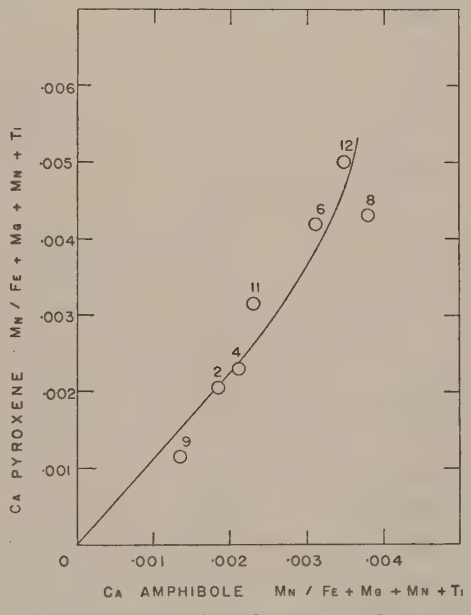


Fig. 7. Distribution of manganese between pyroxene and amphibole.

(2) The distributions are different because of different temperatures of crystallization.

(3) Equilibrium with reference to the distribution of Mn was not established or was not retained in these specimens.

Distribution of Ti

Pyroxene–amphibole (*Fig.* 8). Invariably $X_{Ti}^{amph.} < X_{Ti}^{pyrox.}$, but in one mineral pair which contains relatively small amounts of Ti (specimen 2), the Ti is shared equally by pyroxene and amphibole. The distribution points do not fall on a smooth curve, and a possible cause is noted later.

Amphibole–biotite (*Fig.* 9). The diagram contains some distribution points (marked by crosses) which represent mineral pairs from gneisses. The writer (Kretz, 1959) found that in ten out of fourteen mineral pairs the equation $X_{Ti}^{bi.}/X_{Ti}^{amph.} = 2{\cdot}0$ is very nearly satisfied.

A line has been drawn to pass through points (12), (2) and (9). These represent

mineral pairs in which the amphiboles contain low concentrations of Al, Na, and K. Specimens (10), (6), (3), (4) and (11) are all skarns which contain Al amphiboles. We expect the Ti distribution in these rocks to be the same as in the gneisses, but this is not so. In fact, some skarn amphiboles contain more Ti than the coexisting biotites. Line *B* of unit slope has been drawn to intersect three of these points, but those of specimens (11) and (3) deviate significantly from the line.

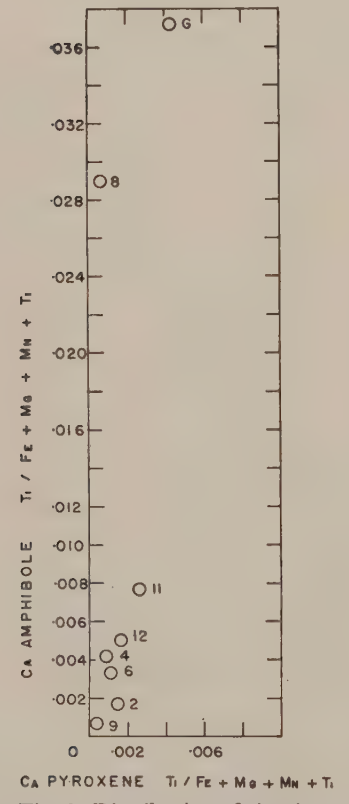


Fig. 8. Distribution of titanium between pyroxene and amphibole.

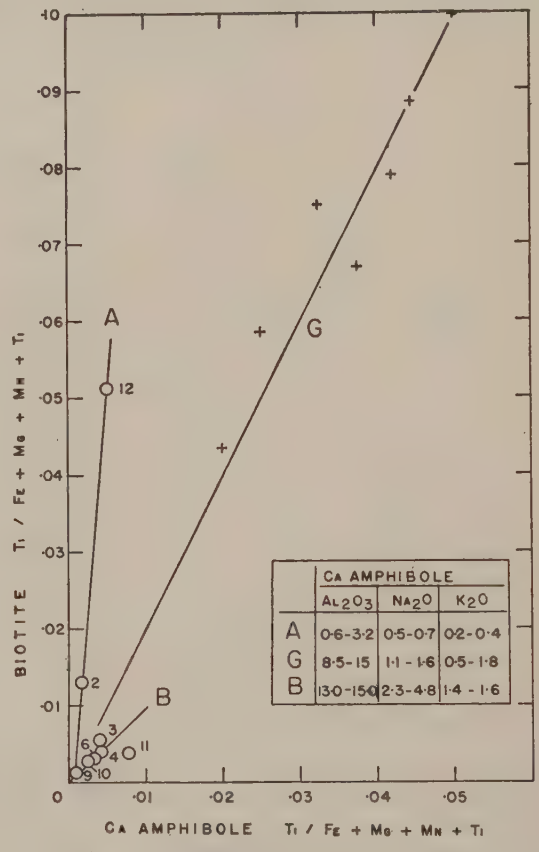


Fig. 9. Distribution of titanium between amphibole and biotite.

The failure of the Ti distribution between biotite and Al amphibole in skarns to be identical to the distribution in gneisses presents a problem similar to that found in connexion with the distribution of Fe between the same minerals. Considering Al amphiboles only, the ratios $X_{Fe}^{amph.}/X_{Fe}^{bi.}$ and $X_{Ti}^{amph.}/X_{Ti}^{bi.}$ are greater in skarn than in gneiss. It was previously suggested that the cause of the difference in Fe distribution may lie in the fact that Al amphiboles from skarns contain higher Na concentrations than Al amphiboles from gneisses (2·17 to 4·8 compared with 1·12 to 1·55% Na_2O). This may also explain the difference in Ti distribution, i.e. an increase of Na content in Al amphiboles increases the affinity of this mineral for both Fe and Ti. More data are needed to test this apparent correlation.

Pyroxene–biotite (*Fig.* 10). All of the distribution points with the exception of those referred to as (11) and (12) fall near a curved line which intersects the origin.

In general, the distribution of Ti in pyroxene–amphibole–biotite is more irregular than the distribution of Mn in the minerals. The cause of this may be that some of the mineral assemblages do not represent an equilibrium condition as far as Ti is concerned, for example specimen (11), Figs. 9 and 10.

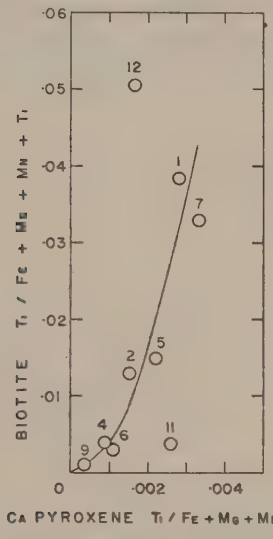


Fig. 10. Distribution of titanium between pyroxene and biotite.

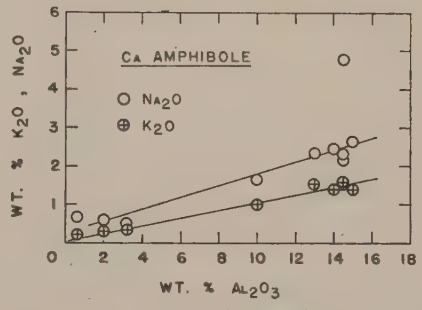


Fig. 11. The sodium and potassium content of amphibole in relation to its aluminium content.

It must be remembered also that Ti ions are quadrivalent and occupy structural sites which are occupied mainly by divalent ions. In relation to the requirement that the charge of an ionic crystal must be balanced, it is expected that the affinity of these minerals for Ti is dependent on the presence of other elements. For example, varying amounts of Al or Na in pyroxene and amphibole may change the affinity of the minerals for Ti. For this reason some scattering of distribution points is to be expected even if equilibrium was attained.

Distribution of Al*

Pyroxene–amphibole–biotite. By examining the mineral analyses it becomes apparent that a correlation exists between the Al content of amphibole and its Na content. A similar correlation exists between the Al content of this mineral and its K content. These relationships are shown in Fig. 11.

It can hardly be expected that these correlations will always be satisfied. The absolute amount of an element in a mineral must primarily be dependent on the availability of the element to the mineral and only secondarily on the concen-

* Weight per cent of the oxides of Al, Na, K, Ba and of V, Zr, Y, Sc are used as measures of concentration. Atomic ratios were not calculated for the first group of elements because the mineral analyses are not sufficiently complete, and for the second group because the structural position of the atoms is not known. Very little or no error is introduced because in the minerals of the present study, the weight per cent of an element oxide is very nearly a linear function of the atomic ratio of the element.

trations of other elements in the mineral. One deviation from the Al–Na correlation is conspicuous in Fig. 11. It is not possible at present to state whether the concentrations of Na and K are dependent on the concentrations of Al, or if the reverse is true.

The distribution of Al between pyroxene and amphibole is shown in Fig. 12. The distribution points fall near a curved line which intersects the origin. The

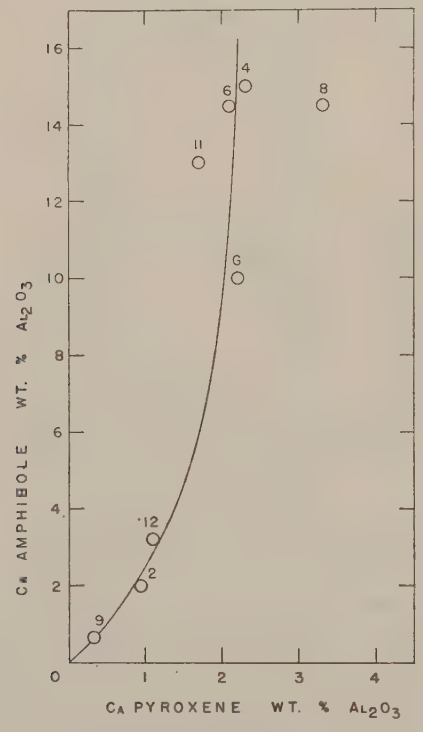


Fig. 12. Distribution of aluminium between pyroxene and amphibole.

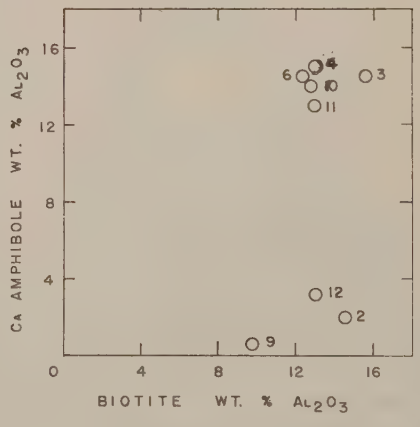


Fig. 13. Distribution of aluminium between amphibole and biotite.

distribution in specimen (8) is conspicuously irregular. Note that the Mn distribution was also irregular in this specimen (Fig. 7).

The distribution of Al between amphibole and biotite is shown in Fig. 13, and between pyroxene and biotite in Fig. 14. The patterns are scattered.

The distribution of Al in pyroxene–amphibole–biotite is even more irregular than the distribution of Ti in these minerals. It is to be expected that the affinity of the minerals for Al is dependent on a large number of factors. Biotite requires a certain amount of Al for its existence. The Al content of amphibole may vary widely, and the large compositional variations that are possible in the 8-co-ordinated positions, $(Ca, Na)_{2-3}$ are likely to affect the mineral's affinity for Al. In contrast, the analysed pyroxenes are rather restricted in Al content. Simple relationships in the distribution of Al are not to be expected, and more work is needed to investigate the effect of all the compositional variables in the minerals on the behaviour of Al.

Distribution of Na

We shall consider now how the Al–Na correlation in amphibole (Fig. 11) is relevant to the distribution of Na in pyroxene–amphibole–biotite.

If the Al content of amphibole is dependent on the Na content (i.e the Na content is the independent variable) then we cannot expect variations of Al content to affect the relationship of $X_{Na}^{pyrox.}$, $X_{Na}^{amph.}$, and $X_{Na}^{bi.}$. Unless other compositional variables have an effect, we should expect simple relationships to appear, as shown by straight lines or curves on the distribution diagrams.

If the Al content of amphibole is the independent variable, the number of Na

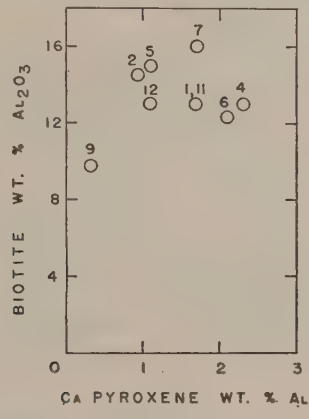


Fig. 14. Distribution of aluminium between pyroxene and biotite.

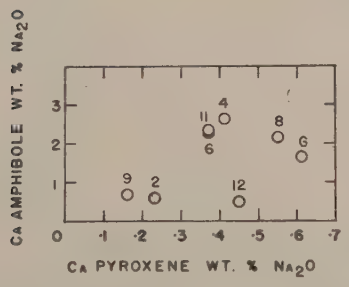


Fig. 15. Distribution of sodium between pyroxene and amphibole.

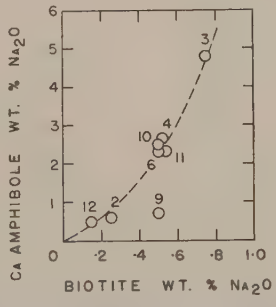


Fig. 16. Distribution of sodium between amphibole and biotite.

atoms which enter this mineral is determined by the number of Al atoms present, and the remaining Na is taken up by the coexisting minerals. Then we cannot expect to find relationships between $X_{Na}^{amph.}$ and $X_{Na}^{pyrox.}$ or $X_{Na}^{amph.}$ and $X_{Na}^{bi.}$, but can expect a relationship between $X_{Na}^{pyrox.}$ and $X_{Na}^{bi.}$.

Amphibole–pyroxene (*Fig.* 15). The pattern is scattered. On the basis of the above discussion one possible factor which may be the cause is that the Na content of amphibole is controlled by the Al content, and thus a simple relationship between $X_{Na}^{amph.}$ and $X_{Na}^{pyrox.}$ is impossible.

Amphibole–biotite (*Fig.* 16). There is an indication that the points fall near a curved line, but more data are needed to determine the reliability of the correlation.

Pyroxene–biotite (*Fig.* 17). The possible dependence of the Na content of amphibole on the Al content of this mineral should have no bearing on the distribution of Na between pyroxene and biotite. We may expect a regular distribution of Na between these minerals regardless of the presence or absence of amphibole.

The distribution points are scattered, and this is explained as follows. Sectors are drawn in Fig. 17 so that the distribution point in sector *A* represents a pyroxene–biotite pair in which the pyroxene has an atomic ratio of Ti within the

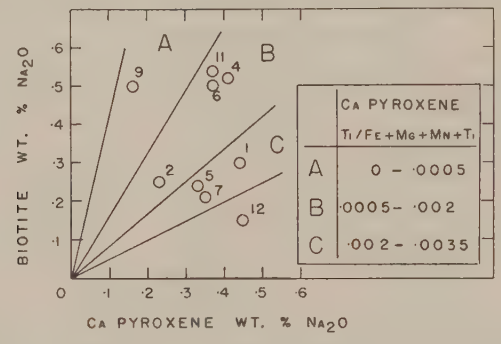


Fig. 17. Distribution of sodium between pyroxene and biotite.

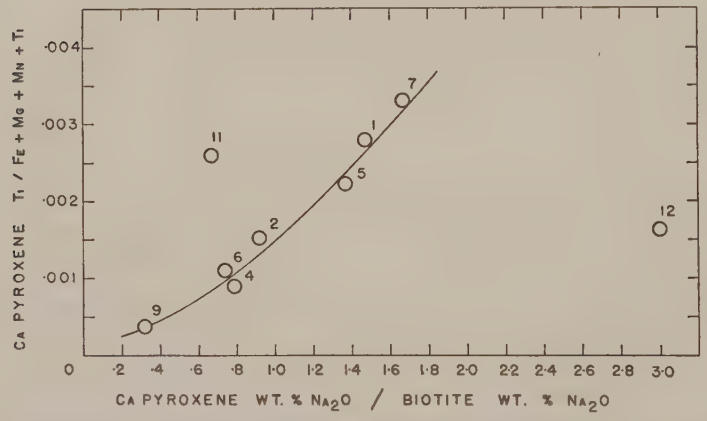


Fig. 18. Relationship between the sodium distribution coefficient in pyroxene–biotite and the atomic ratio of titanium in pyroxene.

range 0·0 to 0·0005. Distribution points that lie in sector *B* represent mineral pairs in which the pyroxenes have atomic ratios of Ti within the range 0·0005 to 0·0020, and those that lie in sector *C* represent mineral pairs in which the pyroxenes have atomic ratios of Ti within the range 0·0020 to 0·0035. If it is supposed that the Na distributions within the concentration range here considered are in agreement with Nernst's distribution law, i.e. the distributions may be graphically expressed by straight lines through the origin, then it becomes evident that the Na distribution coefficient in pyroxene–biotite is a function of the Ti concentration in pyroxene. This relationship is shown in Fig. 18. The mineral pairs of specimens (11) and (12) do not conform to the correlation which exists in the other mineral pairs. The

cause of this will be noted later (p. 24), and these two specimens are for now excluded from the discussion.

Note that an increase of Ti in pyroxene causes this mineral to acquire greater amounts of Na *relative* to the amount of Na in the coexisting biotite, i.e. an increase in the Ti concentration of pyroxene increases its affinity for Na. This implies

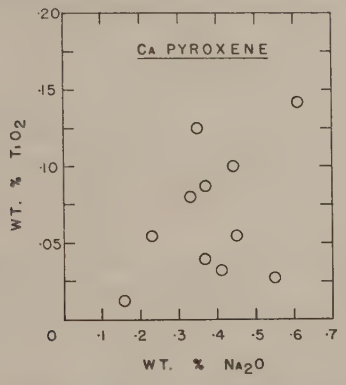


Fig. 19. Graph to show that the titanium and sodium content of pyroxene are not directly related.

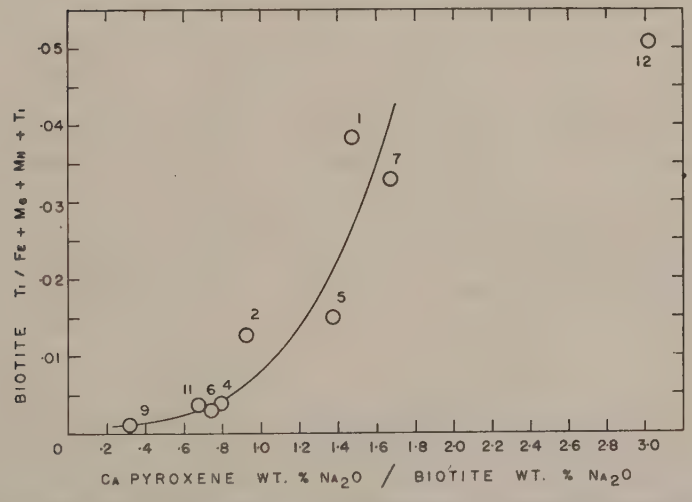


Fig. 20. Relationship between the sodium distribution coefficient in pyroxene–biotite and the atomic ratio of titanium in biotite.

nothing about the absolute amount of Na in pyroxene, or a direct relation between the absolute amount of Ti and Na in pyroxene. Fig. 19 is presented to prove that no direct relationship exists.

Let us recall now that a direct relationship exists between $X_{Ti}^{pyrox.}$ and $X_{Ti}^{bi.}$, which is expressed by a curve on the distribution diagram (Fig. 10). Thus we should expect to find that the Na distribution coefficient $K_{Na}^{pyrox.-bi}$ is related to $X_{Ti}^{bi.}$ as well as to $X_{Ti}^{pyrox.}$. This is confirmed in Fig. 20, which is similar to Fig. 18, except that now the ordinate is the Ti content of biotite rather than pyroxene. A smooth curve has been drawn to best fit the points.

Note that the points deviate somewhat more from a curve than is the case in Fig. 18. This may be caused by the fact that the Ti analyses of biotite are not so precise as the Ti analyses of pyroxene. It was found that the determination of Ti in low concentrations (e.g. in pyroxene) showed a higher degree of reproducibility than the determinations of Ti in higher concentrations (e.g. in biotite). Thus one may infer that the deviations of the distribution points from the Ti distribution curve in Fig. 10 is caused mainly by error in the Ti analyses of biotite. This statement does not apply to points (11) and (12).

So far, specimens (11) and (12), which deviate widely from the $K_{Na}^{pyrox.-bi.}$–$X_{Ti}^{pyrox.}$ correlation (Fig. 18) have not been considered. We note firstly that the Ti distribution between pyroxene and biotite of these specimens is entirely irregular (Fig. 10). It is not surprising therefore that the sharing of Na by these two minerals is also irregular.

Next we observe that whereas point no. (11) deviates from the curve in Fig. 18, it falls near the curve in Fig. 20. This implies that, as far as the Ti concentration of biotite is concerned, the Na is correctly partitioned between this mineral and coexisting pyroxene. The conclusion which follows is that the Ti content of the pyroxene is in error. If $X_{Ti}^{pyrox.}$ is reduced from the determined value of from 0·0026 to 0·0010, the distribution point of specimen (11) in Fig. 10 will shift to the left to join the curve. Also, point (11) in Fig. 18 will be lowered to lie very near to this curve. Thus the Ti content of pyroxene in specimen (11) is too great by a factor of $2\frac{1}{2}$. This indicates that there has been an introduction of Ti to the mineral following the equilibrium crystallization of the rock.

Finally we shall consider skarn no. (12). Note that the Ti distribution between pyroxene and biotite in this specimen is irregular (Fig. 10), and that the $X_{Ti}^{pyrox.}$–$K_{Na}^{pyrox.-bi.}$ relationship is not satisfied (Fig. 18), nor is the $X_{Ti}^{bi.}$–$K_{Na}^{pyrox.-bi.}$ relationship (Fig. 20) satisfactory. The Ti and Na distributions between these two minerals are completely irregular, indicating that an equilibrium between these two minerals with reference to these two elements was not attained or was not retained.

Distribution of K

Pyroxene–amphibole–biotite (*Figs.* 21, 22, 23). The correlation of the K and Al content of the analyses amphiboles has already been noted, and is shown in Fig. 11. As with the Na–Al correlation, it cannot be expected that the K–Al correlation will invariably be satisfied. It may be satisfied only within rather restricted conditions of bulk composition, conditions which evidently existed in the rocks of the present investigation. For example, if there is insufficient K for the relationship of Fig. 11 to be satisfied, or too much K and no coexisting minerals to incorporate the surplus, irregularities will result. However, one may conclude that the data of Fig. 11 indicate that the K content of amphibole is strongly influenced by its Al content. This correlation, together with the fact that biotite requires K for its formation, whereas amphibole and pyroxene do not, removes any possibility of detecting a regular distribution of K amongst the minerals by use of a distribution diagram.

Even though the distribution diagrams are of little value, they are presented (Figs. 21, 22 and 23). They show at least that biotites contain much more *K* than

coexisting amphibole, which is of course expected, and that amphiboles contain considerably more K than coexisting pyroxenes.

Distribution of Ba

Pyroxene–amphibole–biotite. The BaO content of all skarn biotites was found to be greater than 0·50 weight per cent, with one exception (in specimen 9) in which

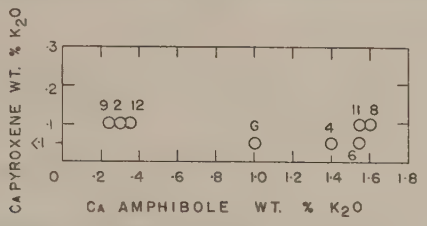


Fig. 21. Distribution of potassium between pyroxene and amphibole.

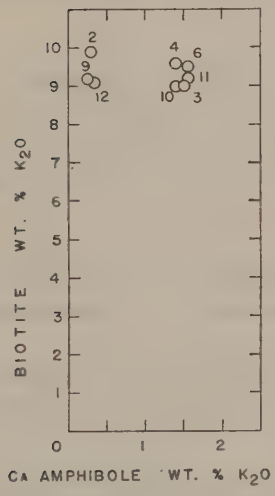


Fig. 22. Distribution of potassium between amphibole and biotite.

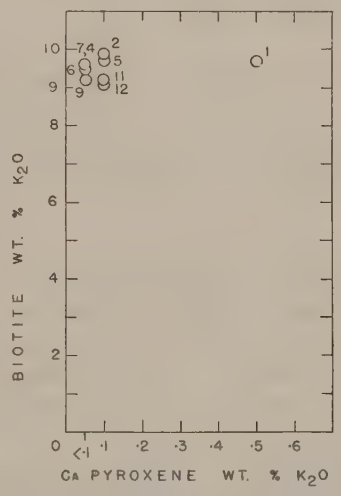


Fig. 23. Distribution of potassium between pyroxene and biotite.

the value is 0·18. The BaO content of the amphiboles ranges from less than 0·01 to 0·037 weight per cent. The three amphiboles which contain low Al concentrations (nos. 2, 9 and 12) tend to have the lowest Ba concentrations. The BaO content of the pyroxenes is, with three exceptions, less than 0·01 weight per cent.

In specimen (2) the ratio (weight per cent BaO in amphibole)/(weight per cent BaO in pyroxene) is 0·79. In general, however, amphibole contains more Ba than coexisting pyroxene. The distribution of Ba amongst coexisting pyroxene, amphibole, and biotite in most rocks follows the formula bitoite > amphibole > pyroxene.

Distribution of V

Pyroxene–amphibole–biotite. In three rocks the ratio (weight per cent V_2O_3 in amphibole)/(weight per cent V_2O_3 in pyroxene) is 2·3, 2·2 and >1·6. The distribution of V between amphibole and biotite in gneisses was previously determined

by the writer (Kretz, 1959): (weight per cent V_2O_3 in amphibole)/(weight per cent V_2O_3 in biotite) = 1·2. In three skarns this ratio was found to be 1·1, >1·7 and >1·2. The distribution of V between pyroxene and biotite in three skarns is (weight per cent V_2O_3 in biotite)/(weight per cent V_2O_3 in pyroxene) = >1·1, 1·7 and >3·5. In general, the distribution of V among pyroxene, amphibole, and biotite follows the formula: amphibole > biotite > pyroxene.

Distribution of Zr, Y *and* Sc

Pyroxene–amphibole–biotite. In three specimens of skarn, amphibole contains slightly more Zr than coexisting pyroxene. In one specimen, biotite contains slightly more Zr than coexisting amphibole.

Yttrium was detected in four amphiboles, but in none of the pyroxenes or biotites.

In one specimen of skarn, the ratio (weight per cent Sc_2O_3 in amphibole)/(weight per cent Sc_2O_3 in pyroxene) = 1·6, and in the specimen of pyroxene–amphibole gneiss this ratio is 1·2.

The Crystal Chemistry of Pyroxene, Amphibole and Biotite in Relation to Element Distribution

The following discussion is a preliminary attempt to correlate the data of element distribution with known properties of atoms and crystal structures.

Previous study

Since the work of Goldschmidt, several attempts have been made to explain the behaviour of elements in terms of ionic size, ionic charge, ionization energy and electronegativity of elements, in relation to mineral structures.

With reference to silicate minerals and the distribution of elements among coexisting minerals, important studies from this viewpoint are by Ramberg (1952b) and DeVore (1955a, b, 1957).

One of the main features of the work of Ramberg and DeVore is a correlation of (1) the electronegativity of oxygen ions in crystals (which increases with increasing polymerization), and (2) the electronegativity of cations (which increases in the order Mg–Fe). Consideration is given to the effect of other anions and cations on the electronegativity of the oxygen ions, and consequently on the distribution of Mg, Fe, etc., among the minerals. For example, in a hypersthene–anthophyllite combination, the mineral with the more electronegative oxygen ions (anthophyllite), will prefer the least electronegative cations namely Mg relative to Fe. The presence of Al in the 4-co-ordinated positions of anthophyllite decreases the electronegativity of the oxygen ions and thus counteracts the mineral's affinity for Mg.

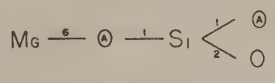
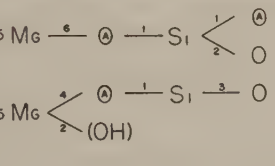
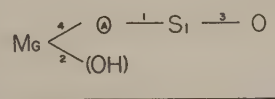
Comparison of pyroxene, amphibole, and biotite crystal structures

The present study is concerned mainly with Fe, Mg, Mn and Ti, elements which evidently occupy 6-co-ordinated positions in pyroxene, amphibole and biotite. The 6-co-ordinated positions are not identical in the three minerals, as can be seen in Table 4. For the purpose of comparing the mineral structures, all occupants of

6-co-ordinated positions are referred to by the symbol Mg, and all occupants of 4-co-ordinated positions by the symbol Si. Oxygen ions which form bonds with only one Si ion are referred to as active oxygen ions, and those that form bonds with two or more Si ions as shared oxygen ions.

In pyroxene, all Mg ions are surrounded by six active oxygen ions, each of which is bound to one Si ion. Each Si ion forms bonds with two active oxygen ions and two shared oxygen ions. A second situation is that found in biotite. Each

Table 4. Six-co-ordinated bonds in pyroxene, amphibole, and biotite.

Ca PYROXENE	
Ca AMPHIBOLE	
BIOTITE	

Mg ion is surrounded by two (OH) ions and four active oxygen ions. Each of these oxygen ions is bound to one Si ion, which in addition is surrounded by three shared oxygen ions. In amphibole there are two kinds of 6-co-ordinated positions; two-fifths are the pyroxene type and three-fifths are the biotite type.

Mineralogical experience has shown that the Al/Si ratio within 4-co-ordinated positions increases in the order pyroxene–amphibole–biotite. In biotite this ratio must be 1 : 3 or greater.

Thus we see that the order pyroxene–amphibole–biotite is one of progressive change. The change involves:

(1) A decrease in the number of active oxygen ions, i.e. an increase of polymerization.

(2) An increase of (OH) positions.

(3) An increase of the Al/Si ratio in 4-co-ordinated positions.

In addition, it may be mentioned that there is a progressive decrease in the ratio: (8-co-ordinated positions in pyroxene and amphibole or 12-co-ordinated positions in biotite)/(6-co-ordinated positions). This ratio ranges from 1 : 1 in pyroxene to (1–1½) : 2½ in amphibole to 1 : 3 in biotite.

Structural considerations alone lead us to expect that elements will be distributed among pyroxene, amphibole, and biotite according to the formula pyroxene > amphibole > biotite or biotite > amphibole > pyroxene.

Crystal chemistry of the skarn minerals

Iron. As noted above, the order pyroxene–amphibole–biotite is one of increasing polymerization. In most skarns this is also a sequence of increasing Al concentration. Since the effects of these two factors on the electronegativity of oxygen ions are contrary, it is difficult to predict the Fe–Mg distribution among these minerals on the basis of the electronegativity principle. However, three skarns contain pyroxene–amphibole combinations in which the amphiboles contain very low concentrations of Al. Here we would expect to find a greater Fe/(Fe + Mg) ratio in pyroxene than in amphibole. Observe (Fig. 2) that Fe is approximately equally distributed between the two minerals.

A tentative correlation was made between the Al content of pyroxene and its affinity for Fe (Fig. 4). This correlation is in agreement with the electronegativity principle. It was found that the Al, Na or K content of amphibole affects its affinity for Fe (Figs. 2 and 3). In the case that the Al content is the dominant influence the results are in agreement with the electronegativity principle. If the Na or K content of amphibole has an influence on its affinity for Fe, this may be attributed to a decrease of the electronegativity of the oxygen ions by a substitution of less electronegative Na or K ions for more electronegative Ca ions.

Manganese. The general formula for the distribution of Mn is pyroxene > amphibole > biotite. The electronegativity of Mn^{2+} is 1·4, as compared with 1·2 for Mg^{2+} and 1·65 for Fe^{2+}. Disregarding the effect of Al, we expect Mn to be preferred by biotite rather than pyroxene, which was not found.

The size of the Mn ion may be important in determining its behaviour. It is considerably larger than Fe^{2+} and Mg^{2+} (0·91 compared with 0·83 and 0·78 Å radius) and is not much smaller than Ca (1·06 Å). The Mn ion may form a more stable bond in minerals which contain 8-co-ordinated positions, in which case the observed distributions may be partly explained in terms of ionic size.

It would be gratifying if one could explain why the distribution of Mn in amphibole–biotite is a linear relationship, whereas the distribution in pyroxene–amphibole and pyroxene–biotite is non-linear. At present it appears to be most difficult to find a quantitative correlation of the observed distribution coefficients with properties of Mn ions or properties of the crystal structures.

It is important to note that a regular Mn distribution between pyroxene and biotite persists to low concentrations of Mn, with values of $X_{Mn}^{pyrox.}$ in the order of 0·001 and X_{Mn}^{bi} in the order of 0·0003. Mn is regularly distributed between the two minerals even when its concentration in biotite is in the order of three atoms of Mn per 10,000 atoms of (Mg + Fe + Mn + Ti), or three atoms of Mn per 70,000 atoms of all kinds in the crystal. On thermodynamic grounds, the regular distribution of an element at very low concentrations is to be expected*, but on

* This is so because of the great change of chemical potential which accompanies small changes of concentration of an element when these changes occur at low concentrations.

grounds of crystal chemistry the regular partitioning of a few atoms between two minerals which contain in proportion tens of thousands of other atoms is incredible.

Titanium. The distribution of Ti among the minerals was found in general to be biotite > amphibole > pyroxene. The electronegativity of Ti^{4+} is 1·6, i.e. nearly the same as Fe^{2+}. Neglecting the effect of Al, we expect on the basis of this value alone, that Ti is preferred by pyroxene rather than by biotite. However, we may expect that the high charge number of Ti^{4+} has a much stronger influence in determining the behaviour of this element. The placing of Ti in 6-co-ordinated positions requires a decrease in the charge of other parts of the crystal e.g. placing of Na^{+} in 8-co-ordinated positions or Al^{3+} in 4-co-ordinated positions. The fact that the minerals which contain the highest Al concentration contain the highest Ti concentration may be significant in this regard. Additional evidence is found in the observed increase in the affinity of amphibole for Ti which can be attributed to an increase of its Al, Na and K content (Fig. 9).

Sodium. We now refer to the distribution of Na between pyroxene and biotite, and the correlation of this distribution with the Ti content of both minerals. An increase in the Ti content of pyroxene is correlated with an increase in the affinity of this mineral for Na. One may attempt an explanation of this by noting that the charge of pyroxene remains neutral if the substitution of one Ti^{4+} for one $(Mg, Fe)^{2+}$ is accompanied by the substitution of two Na^{+} for two Ca^{2+}. If the affinity of pyroxene for Na is increased by this method alone, we should expect a direct correlation between the number of Na ions in pyroxene and the number of Ti ions present. But no correlation of this kind exists (Fig. 19), and the observed relationship is not simply a matter of Na ions accompanying Ti ions.

It is important to note again that the Na content of one phase is regularly related to the Na content of the coexisting phase even when the concentrations are very low. A calculation has been made to show that the relationship persists when three atoms of Na are present in biotite per 1000 (K + Ca + Na + Ba) atoms, or three atoms of Na per 20,000 atoms of all kinds in the crystal. Furthermore, the Na distribution coefficient is greatly changed by small variations in dilute concentrations of Ti in the minerals. This change is caused by variations in the order of from five atoms to forty atoms of Ti per 10,000 (Mg + Fe + Mn + Ti) atoms within pyroxene, or five atoms to forty atoms of Ti per 100,000 atoms of all kinds in the crystal. A few atoms of Ti amongst tens of thousands of other atoms in the pyroxene and biotite crystals will determine quantitatively how a few atoms of Na are shared by the two crystals. Such features must be of extreme importance in relation to the nature of atomic bonds in the crystals, and are difficult to explain in terms of the present resources of crystal chemistry.

With reference to ions and crystal structures the writer concludes only that regular distributions of elements indicate that these elements occupy structural sites in the minerals. The behaviour of elements in crystals is determined by bond energies, which are dependent on fundamental properties of atoms and on the arrangement of atoms in crystals, as well as temperature and pressure. Evidently the properties of atoms such as ionic radius, ionic charge, and electronegativity are not sufficient measures of bond energy. A fine understanding of element behaviour is not possible until more is known about atomic bonds in crystals.

Conclusion

On theoretical grounds we expect that when two minerals of variable composition coexist in a rock, there will be a certain consistency or regularity in the distribution of the elements between the minerals. The expectation is based entirely on the familiar and important concept of equilibrium. If equilibrium is attained within small volumes of rock and if no chemical changes occur following the quenching of the rock, we should be able to detect the various relationships which characterize an equilibrium.

The present study was an attempt to find some regular relationships among the elemental compositions of pyroxene, amphibole and biotite. The atomic structure of the minerals is complex, and the number of elements which occur in variable amounts is large. Even so, some regular relationships have appeared, and these are taken as indications that the minerals of each assemblage have experienced a time of chemical communication and chemical equilibrium. However, certain elements appear to be irregularly distributed among the minerals. In view of the large number of compositional variables in each mineral, this is perhaps to be expected. The partial or complete irregularities do not necessarily indicate that an equilibrium was never attained; more likely they indicate that much more exploration is necessary to discover the interrelationships among the numerous compositional variables.

Again on theoretical grounds, we expect that a distribution coefficient may be a function of temperature. Since we seldom know the equilibration temperature of a rock, another variable is introduced. Preliminary evaluations of the temperature effect may come from the study of natural mineral assemblages, but eventually must come from experimental studies. It will not be surprising however, to find that with reference to certain elements and certain minerals, the temperature effect is negligibly small. With reference to these elements and phases it may be possible to determine the distribution coefficients more accurately by the study of natural mineral assemblages than by the study of synthetic mineral assemblages.

Once the distribution coefficients are established, the complex and interesting problem remains, to explain in terms of atomic properties and crystal structures why a distribution coefficient is a particular value, and not another value. Some progress has been made in this direction, but some of the problems which remain seem at present, insurmountable.

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On the marine geochemistry of barium

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A number of questions involving the geochemical behaviour of barium in the marine domains has prompted us to ascertain the barium content of sea water as a function of depth, inasmuch as previous analyses, which dealt mostly with surface Atlantic waters, have only revealed with one exception the upper limit of barium concentrations (Table 1).

Table 1. Previous investigations of the barium content of marine waters

Location	Depths (m)	Barium concentration (μg/l.)	Reference
English Channel	70	<200	Orton (1924)
Irminger Sea	2900	<(30–90)	von Englehardt (1936)
North Sea	0	<(30–90)	von Englehardt (1936)
West Scottish Coast	0	<100	Black and Mitchell (1952)
English Channel	0	6·2	Bowen (1956)

In the first place, is the depth distribution of barium in sea water similar to that of radium? On the basis of their chemical and physical characters, these two elements should follow each other in nature. Koczy (1958) has published an extensive study of depth profiles of radium in sea water which could be used as a basis of comparison. Secondly, how closely do barium concentrations approach a state of saturation in sea water with respect to precipitation of barium sulphate? Finally, it has been pointed out repeatedly that barium concentrations in pelagic sediments underlying biologically productive oceanic areas are unusually high (Revelle *et al.*, 1955; Goldberg and Arrhenius, 1958; Goldberg, 1960). If so, is there any correlation between the biological phenomena and the barium distribution in marine waters?

Method

The barium was assayed by isotope dilution technique using the 60° sector single focusing mass spectrometer with a 12 in. radius of curvature at the California Institute of Technology. An enriched barium-135 spike, obtained from the Oak Ridge National Laboratory, was dissolved in 5% nitric acid to make up a standard solution containing 0·45 mg of barium per ml. The isotopic compositions of the spike and of "common barium" were determined (Table 2).

Sea water (100 ml) was introduced into a 250 ml beaker, and 100 μl of the barium spike were then added. The combined solutions were taken to dryness. The

soluble alkali salts were leached from the precipitate with distilled water. The remaining solids, including barium in the form of sulphate, were transferred to a 1 ml centrifuge tube and washed several times with distilled water. About 5 μg of the barium sulphate were placed on the surface of a tantalum filament which had been carefully baked in a vacuum at elevated temperature to remove any barium initially present on the surface.

Table 2. Isotopic composition of common barium and the barium spike (Units in atom %.)

Isotope	130	132	134	135	136	137	138
Spike barium	0·02	0·03	1·48	67·32	12·35	5·63	13·17
Common barium	0·12	0·10	2·44	6·62	7·87	11·25	71·60

The spectrometric procedure has been described by Chow and McKinney (1958). The filament current was slowly raised to 2 A, corresponding to a temperature of about 1500°C. At this temperature only the Ba^+ spectrum was observed. The BaO^+ and the BaO_2^+ peaks occurred at much lower filament temperatures. The amount of barium in the sample was calculated from the following equation:

$$M = \frac{m(Ba_s^{135} - N \times Ba_s^{138})}{N \times Ba_w^{138} - Ba_w^{135}}$$

where M = barium in the sample (μg);
m = amount of spike added (μg);
N = observed Ba^{135}/Ba^{138} ratio;
Ba_s^{135}, Ba_s^{138} = percentage of Ba^{135} and Ba^{138} in the spike, respectively;
Ba_w^{135}, Ba_w^{138} = percentage of Ba^{135} and Ba^{138} in the common barium, respectively.

Results

The barium profiles for four Pacific Ocean stations are given in Table 3. The probable error of the analyses is about 3 per cent. It is quite clear that at all

Table 3. The barium concentrations in Pacific Ocean waters (Stations are from the Downwind Expedition of the Scripps Institution of Oceanography, October, 1957 to February, 1958.)

Station	Downwind 6		Downwind 7		Downwind 8		Downwind 17	
Latitude	11° 00′ N		07° 08′ N		03° 14′ N		34° 50′ S	
Longitude	128° 30′ W		129° 16′ W		130° 31′ W		135° 53′ W	
	Depth (m)	Ba (μg/l.)	Depth (m)	Ba (μg/l.)	Depth (m)	Ba (μg/l.)	Depth (m)	Ba (μg/l.)
	0	12	705	32	0	12	4	10
	2698	32	3107	43	517	16	518	12
	4752	46	4323	51	1051	31	865	12
					2167	29	1937	27
					3002	43	3470	28
					4392	63	4185	30

stations there is an increase in barium content with depth. The waters were unfiltered and had been stored in acid leached Pyrex bottles with wax-sealed polyethylene stoppers for a period of approximately 2 years at a temperature slightly above 5°C. Possible loss of barium from solution by sorption on the glass walls or dissolution from the glass, if any, would most probably introduce a small, constant and additive error to all of the results.

Discussion

The depth distribution of barium is similar to that of radium (Fig. 1). Koczy (1958) postulates that the radium originates from the radioactive decay of its

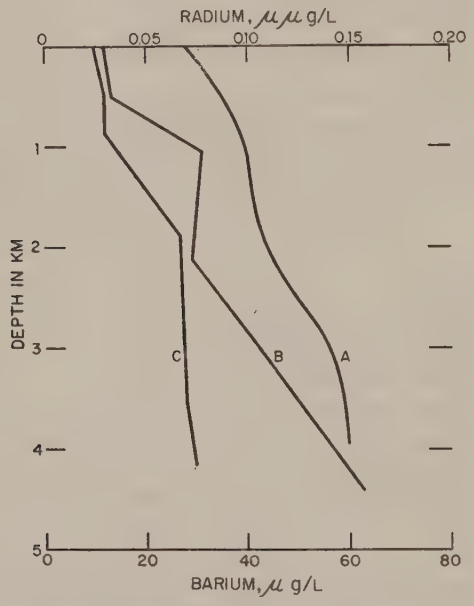

Fig. 1. Barium and radium profiles in sea water. (a) Radium from Swedish Deep Sea Expedition No. 102. Radium values from Koczy, 1958. (b) Barium from Downwind Station 8. (c) Barium from Downwind Station 17.

parent ionium in the sediments and subsequently diffuses upward through the water column. However, where radium doubles its concentration from the surface to 4000 m, barium, in an adjacent station, shows a fivefold increase over the same depth range.

The degree of saturation of barium in sea water can be approached in the following way. Barium in solution probably exists in two principle forms, divalent barium ion and the undissociated barium sulphate. The solubility product of barium sulphate at 25°C and a pressure of 1 atm is of the order of 10^{-10} (Bjerrum *et al.*, 1958). The dissociation constants of all divalent ions cluster about 0·005 for the undissociated soluble sulphates (Robinson and Stokes, 1955). The sulphate concentration in sea water is 28 mM, while the activity coefficients of di-divalent salts can be assigned the value of 0·1 for solutions with an ionic strength

of 0·7, similar to that of sea water (LATIMER, 1952). An activity coefficient of 1·0 is taken for the undissociated barium sulphate. Thus,

$$[Ba^{2+}][SO_4^{2-}] = 10^{-10}$$

$$(Ba^{+2}) = 3{\cdot}6 \times 10^{-7}\ M$$

$$= 49\ \mu g/l.$$

and

$$\frac{[Ba^{+2}][SO_4^{2-}]}{[BaSO_4]_{undiss.}} = 5 \times 10^{-3}$$

$$(BaSO_4)_{undiss.} = 2 \times 10^{-8}\ M$$

$$Ba \text{ in } (BaSO_4)_{undiss.} = 2{\cdot}7\ \mu g/l.$$

Hence, for a total soluble barium concentration of around 52 μg/l., 5 per cent is in the undissociated form.

Other possible ionic associations of barium with such anions as phosphate,

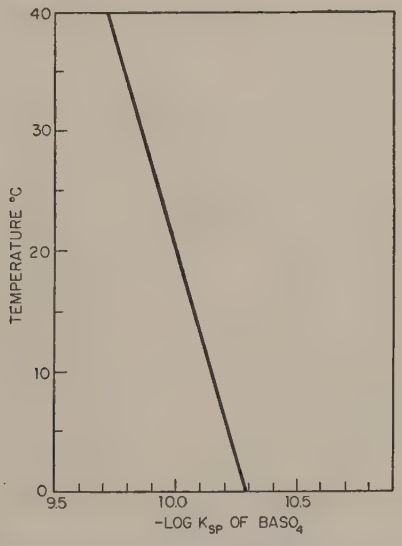

Fig. 2. The dependence of the solubility product of barium sulphate upon temperature.

bicarbonate, carbonate, hydroxide and silicate have been neglected for two reasons: (1) these anions are less abundant than sulphate and would have a consequentially smaller role in delimiting the total dissolved barium concentration in sea water; and (2) the stability constants of such ion pairs are yet to be determined.

More consequential to the saturation concentration of barium sulphate in sea water, however, is the pressure and temperature dependence of the solubility product. The temperature dependence of the solubility product is shown in Fig. 2 which is calculated from data in BJERRUM *et al.* (1958). It is readily seen that at one atmosphere, a change of temperature from 25°C to 0°C results in a decrease of the solubility product by over a factor of 2.

Owen and Brinkley (1941) have tabulated the necessary data from which the effect of pressure on the barium sulphate solubility product in sea water can be considered. Neglecting the pressure effect upon partial molal volumes, which is a second-order term for pressure up to 500 atm

$$RT \ln K^P/K = -\Delta\bar{V}(P - 1)$$

where K^P and K are the solubility products at pressure P and 1 atm, respectively, and $\Delta\bar{V}$ is the difference in partial molal volumes at 1 atm between barium ion plus sulphate ion and barium sulphate. At a pressure of 500 atm, $\Delta\bar{V}$ has a value of -42 ml and hence K^P/K can be calculated from the above equation to have a

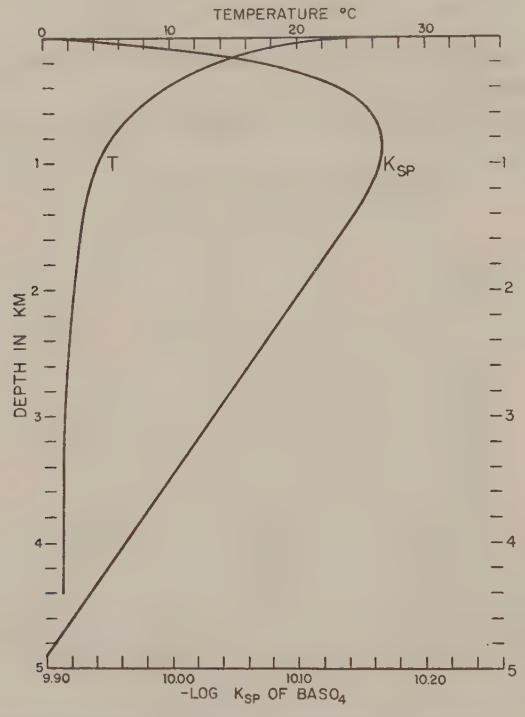

Fig. 3. The temperature profile of Downwind Station 8 and the corresponding depth profile of the solubility product of barium sulphate corrected for temperature and depth.

value of 2·5, i.e. the pressure effect upon the saturation value of barium ion, assuming constant sulphate concentration, results in a value 2·5-fold greater at depths around 5000 m than at the surface.

The pressure and temperature effects may be combined, as illustrated in Fig. 3 for the Downwind Station 8, to show a minimum in the saturation value of barium ion as a function of depth in the oceans. The initial decrease in barium ion concentration with depth reflects the temperature effect, while below the thermocline the subsequent increase mirrors the pressure effect. It should be pointed out that we have not taken into consideration changes in activity coefficients with

either temperature or pressure and the pressure effect on the temperature dependence of K_{sp}.

Notwithstanding these uncertainties in the above computations, it is evident that the saturation values of barium are not approached in surface ocean waters but may be reached at greater depths. Note the value of 63 μg/l. at Downwind Station 8 at 4392 m and the predicted value of about 70 μg/l. from Fig. 3.

Finally, we may seek out the mechanisms governing the depth distribution of barium. The similarity of the barium curve with those of the nutrient species such as phosphate, silicate and nitrate suggests a correlation between barium and the biochemical cycles in the seas. Several possibilities exist.

During the oxidation of detrital organic matter as it falls from the surface to deeper layers of the oceans, high levels of sulphate ion can be presumed to exist in the organic microenvironment. Therefore a subsequent precipitation of barium sulphate could occur. As the organic matter is further oxidized, the microenvironment is destroyed. Then, the precipitated barium sulphate may dissolve and return to solution. The net effect of such processes is the transference of barium from surface to depths.

We may also consider a direct transfer of barium by organisms from surface to deeper waters. BOWEN (1956) has reported an enrichment of barium in the dry organisms over sea water by factors of from 450 to 4400 in a suite of specimens which includes brown, red and green algae, chiton shells, cephalopod bone, mollusc shells and corals. As organisms die or as plants fall out of the euphotic zone, the decaying remnants can furnish barium ions to the sea water. If such a mechanism is an important conveyor of barium to deeper waters, other ions such as copper, nickel, vanadium and cobalt, which are highly enriched in organisms, may show similar depth distributions to those of barium.

Finally, we can not completely disregard the regeneration of barium from the sea floor. As it decomposes, organic debris on the ocean bottom can supply barium to waters overlying the sediments. If barium is in such solid phases as barite (GOLDBERG and ARRHENIUS, 1958), contact of such materials with any undersaturated bottom waters may result in dissolution of the barium sulphate. However, at the present time it is extremely difficult to assess such contributions in relation to those transported downward by the marine biosphere.

Acknowledgements—We are indebted to Dr. CLAIRE PATTERSON of the California Institute of Technology who provided the stimulation for this work as well as the use of the mass spectrometer and to Mr. F. T. MANHEIM of the Geological Survey of Sweden whose refined spectrographic techniques confirmed the observed increase in barium with depth in seawater. This work was supported by the Division of Biology and Medicine, U.S. Atomic Energy Commission, under a contract with the University of California at La Jolla.

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Trace and minor elements in Woodbine sub-surface waters of the East Texas basin*

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Abstract—As the first phase of an investigation of the possible geologic significance of the occurrence and distribution of trace and minor elements in deep sub-surface waters, determinations have been made of these elements in a number of water samples from the Woodbine sand of Upper Cretaceous age in the East Texas basin. The determinations were made by use of an emission spectrograph.

Of a number of elements which occur in trace amounts in Woodbine waters, four appear to vary systematically in concentration. Strontium and potassium increase in concentration with increasing depth from which the water samples were produced. The distribution of barium, which occurs in relatively high concentrations in the waters of the north-western part of the basin, seems to be related to the pattern of deposition of near-shore sediments during a part of Woodbine time. The distribution of manganese, which is found in relatively high concentrations in the central portions of the basin, appears to reflect the areal extent of deeper parts of the basin. The occurrence of soluble manganese in this area indicates that reducing conditions have prevailed in the central part of the basin during the past.

Introduction

The literature of geochemistry contains numerous speculations as to the geologic significance of trace elements in sediments. Although there have been very few references to the possible significance of trace and minor elements† in sub-surface waters, it might also be considered that these, too, may yield information of geologic interest. With this thought in mind, research was initiated on the occurrence of trace and minor elements in sub-surface waters and on the distribution of these elements in sedimentary basins. An emission spectrograph was used in this work.

Fortunately, a number of sub-surface water samples were on hand to utilize in this investigation. These had been collected some years ago by careful sampling of water produced on drill stem tests. The samples were obtained from several formations in the Gulf coast of the United States, and information was compiled at the time of their collection on their hydrocarbon contents and certain major inorganic constituents (Buckley *et al.*, 1958). A particularly good geographical array of samples was secured from the Woodbine sand of the East Texas basin. Since it was realized at the time these samples were collected that they would probably be utilized for future detailed examination, they were stored carefully in glass bottles.

As the first phase of an investigation of the possible geologic significance of

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† The distinction between "trace" and "minor" elements is primarily one of degree. Trace elements are those which are present in very small amounts, usually in concentrations of the order of a few parts or of tens of parts per million; minor elements are those which usually are present in concentrations of the order of hundreds or thousands of parts per million. The above definitions are used in this paper; they apply particularly to the type samples with which this paper is concerned (concentrated brines). The distinction between trace and minor elements is by no means clear-cut, and the terms are sometimes used synonymously.

trace and minor elements in sub-surface waters, attention has been given to Woodbine waters from the East Texas basin. The approach has consisted of determining qualitatively all elements possible, and of attempting to relate the distribution of these elements to recognizable geologic features of the Woodbine basin. Quantitative analyses were then made of those elements which appeared to vary systematically in concentration. The research is thus exploratory, with the objective of determining what elements may be of geologic interest, and in what ways their distributions are affected by the geology of the basin.

Experimental Procedure

The spectrograph used in minor and trace element determinations is a Jarrell Ash 3·4 m stigmatic grating instrument with a 6 in. concave, 15,000 line/in. reflection grating in a Wadsworth mounting. Emission of light from a sample may be achieved by use either of a direct current arc, of an alternating current arc, or of an intermittent spark. A spark source was used in all work with sub-surface water samples.

After various procedures had been tried for burning of the inorganic constituents of typical sub-surface waters, a simplified method was evolved which entailed no prior concentration or evaporation of the water sample. In this method, a small volume of the sample (together with a smaller volume of a solution of an internal standard if quantitative results be desired) is placed in a small, shallow porcelain vessel. A thin disk of slightly porous carbon, rotated at a slow speed by an electric motor, is allowed to dip into the sample and to become saturated with it. The disk forms the bottom electrode of the pair between which sparks are formed. Rotation of the disk ensures a uniform introduction into the spark of the constituents of the water sample.. The top electrode is a porous cup of carbon into which distilled water is placed. This method is not only simple and rapid, but it also produces reproducible results with a minimum amount of interference resulting from the formation of cyanogen spectral bands. The latter interference is usually very troublesome in any spectrographic method which employs carbon electrodes.

In order to obtain reproducible results suitable for quantitative interpretation, it was found necessary that sparking conditions and settings of the various adjustments provided on the spectrograph be maintained under close control.

The spark excitation conditions and settings given in the following table were used in all work with sub-surface waters:

Number of spark breaks per half cycle	>10
Inductance of source	625 μH
Capacitance	0·0025 μF
Primary resistance	15 Ω
Secondary resistance	Residual
Powerstat setting	225 V
Current	3·25 A
Exposure time	2 min
Slit width	20 μ
Slit height	1·5 mm
Analytical gap	4 mm
Auxiliary gap	7·5 mm

The photographic plates on which spectra are recorded are large enough to permit a number of different spectra to be exposed on each plate. For wavelength calibration of the spectral lines, several comparison spectra of an iron arc were usually included on each plate. Use of reproducible conditions in producing the spectra of the samples allowed comparison of the intensities of the spectral lines of various elements and thus permitted estimation of the relative amounts of various elements present in the samples.

For the quantitative analysis of particular elements present in the samples, use was made of elemental internal standards which were added to the samples before burning. A preliminary examination of the elements present in Woodbine sub-surface waters demonstrated that rubidium and chromium were absent. These elements were accordingly used as internal standards and were added in amounts sufficient to yield concentrations in the samples of 1000 p.p.m. rubidium and 800 p.p.m. chromium.

A microdensitometer was used to measure the intensities of the spectral lines of the internal standards and of those elements for which quantitative results were desired. By reference to "working" curves relating intensity to concentration, it was possible to determine concentrations of various elements present in the water samples with an uncertainty of about ± 5 per cent. The "working" curves were prepared using solutions which contained the elements of interest and had a Na^{+1} concentration of 20,000 p.p.m. The high Na^{+1} concentration was used for the synthetic solutions so the matrix effect in the natural and synthetic solutions would be constant.

Samples Utilized

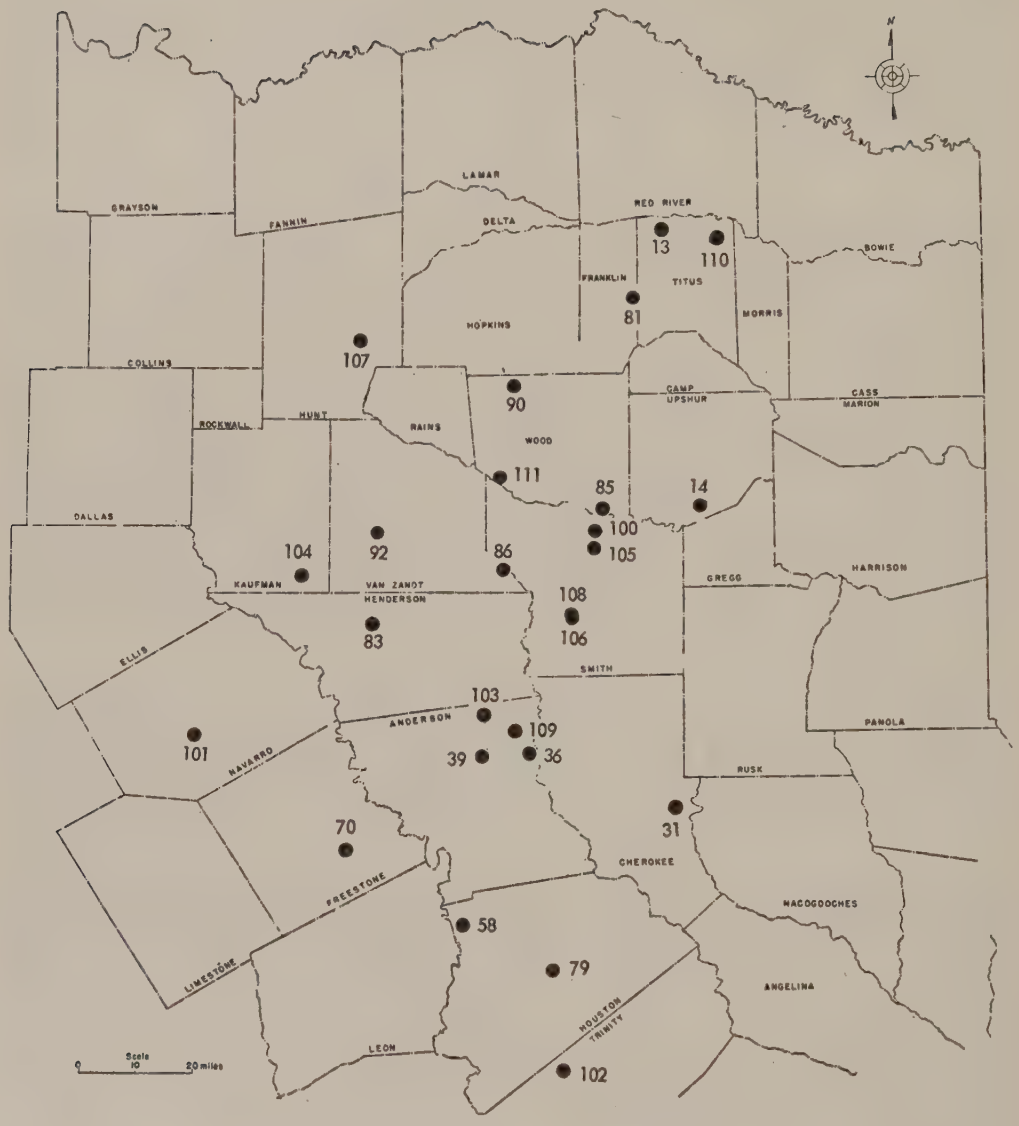
The geographical locations of the wells from which the Woodbine water samples were obtained are shown in Fig. 1. Most of the samples came from the Dexter member of the Woodbine; in some cases, however, the Dexter and Lewisville members were not differentiated. The Woodbine formation is of Upper Cretaceous age.

As shown by previous work (Buckley *et al.*, 1958) on the major constituents of the samples, chloride was the principal anion present, and the predominant cation was sodium. Other cations, present in smaller amounts, were calcium and magnesium. A significant feature of the results of the previous work was the dependency of salinity on depth. This relationship is shown in Fig. 2, which illustrates the increase of chloride concentration with increasing sub-sea depth. A possible explanation of the break in the curve which occurs at a depth of about 5000 ft is that most of the samples which were produced at depths in excess of about 5500 ft came from the southern part of the basin, an area which has presumably been downwarped.

Results

Qualitative analysis

Table 1 shows the presence or absence and relative abundance of nickel, zinc, silver, copper, iron, titanium, aluminium, lithium, rubidium, chromium, vanadium and beryllium in Woodbine sub-surface waters. The concentrations of these elements were not determined quantitatively either because there was an apparent



EAST TEXAS AREA

Fig. 1. Location of wells from which samples obtained.

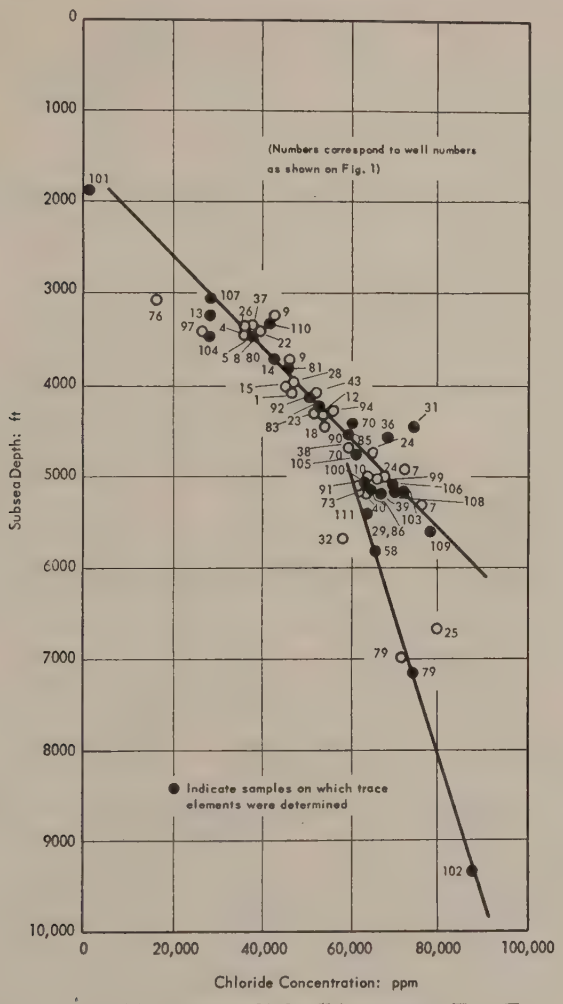


Fig. 2. Chloride content of Woodbine waters, East Texas area.

lack of variation in concentration from sample to sample, or else because any differences in concentration did not appear to show systematic variation from sample to sample.

An element which might possibly vary systematically in concentration is nickel. Fig. 3 illustrates the distribution of nickel (using the symbols for relative concentrations from Table 1) within the East Texas area, and locations of principal oil fields. In most instances it is observed that water samples containing lowest concentration of nickel were taken from wells either near or adjacent to Woodbine oil production.

Quantitative analysis

The relative concentrations of each of four elements—strontium, potassium, barium and manganese—appeared to exhibit systematic variations from sample

Table 1. Results of qualitative analysis of Woodbine waters

Well number*	Sampling depth (Ftsub-sea)	Nickel†	Zinc†	Silver†	Copper†	Iron†	Titanium†	Aluminium†	Lithium†	Rubidium†	Chromium†	Vanadium†	Beryllium†
101	1886–1902	M	M	A	M	M	M	A	A	A	A	A	A
107	3044–3086	W	M	A	M	M	M	A	A	A	A	A	A
13	3212–3262	M	A	A	M	A	A	W	A	A	A	A	A
110	3353–3371	M	W	A	M	M	M	A	A	A	A	A	A
104	3431–3451	A	A	A	M	M	M	A	A	A	A	A	A
14	3712–3824	W	A	A	W	A	A	A	A	A	A	A	A
81	3726–3777	W	A	A	W	A	A	W	A	A	A	A	A
92	4088–4143	S	W	A	M	M	M	S	A	A	A	A	A
83	4236–4255	M	A	A	M	A	A	A	A	A	A	A	A
70	4403–4433	S	W	A	S	A	A	M	A	A	A	A	A
90	4408–4463	W	W	A	W	M	M	W	A	A	A	A	A
31	4450	M	M	A	M	A	A	A	A	A	A	A	A
85	4474–4543	W	M	A	M	M	M	W	A	A	A	A	A
36	4550	A	A	A	A	W	A	W	A	A	A	A	A
105	4760–4783	S	A	A	M	M	M	A	A	A	A	A	A
100	4964–5035	M	M	A	M	M	M	A	A	A	A	A	A
106	5103–5125	S	W	A	S	M	M	W	A	A	A	A	A
86	5118–5169	W	W	A	M	M	M	W	A	A	A	A	A
108	5135–5173	S	S	A	S	M	M	A	A	A	A	A	A
39	5180	W	A	A	A	A	A	W	A	A	A	A	A
103	5138–5203	S	S	A	M	M	M	A	A	A	A	A	A
111	5391–5406	S	W	A	M	M	M	A	A	A	A	A	A
109	5586–5608	S	W	M	M	M	M	A	A	A	A	A	A
58	5780–5827	W	W	A	M	M	M	W	A	A	A	A	A
79	7133–7151	M	A	A	W	A	A	A	A	A	A	A	A
102	9341–9371	W	S	A	M	M	M	A	A	A	A	A	A

* The well numbers correspond to the numbers which are found on the map shown as Fig. 1.

† Symbols refer to relative intensity of certain spectral lines. Order of decreasing intensity is: S > M > W > A.

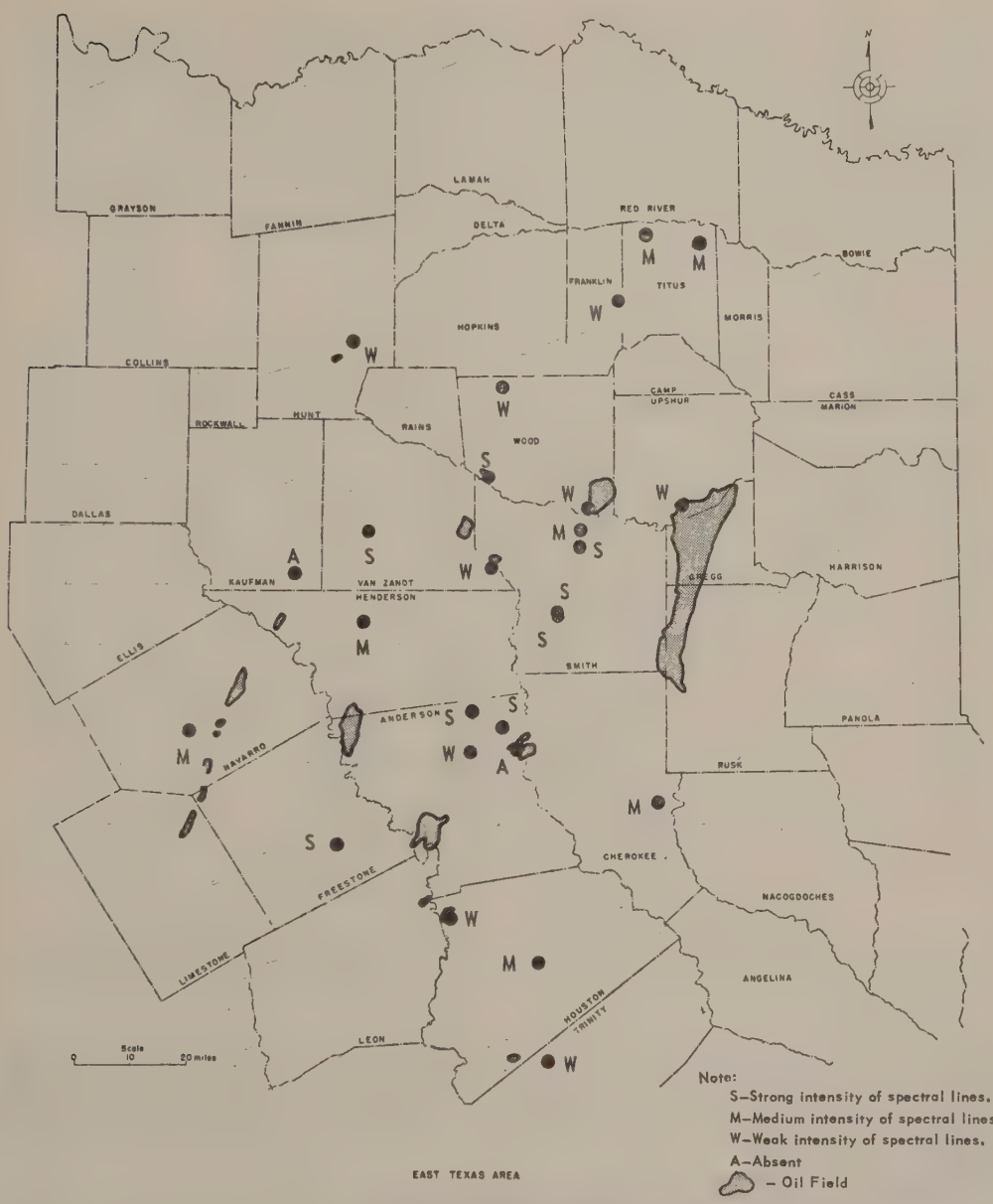


Fig. 3. Nickel content of Woodbine waters.

to sample. In order to investigate further these variations, quantitative analyses were made for each of these elements by the procedure outlined in a preceding section. The results obtained and the nature of the variations are discussed in the following paragraphs for each of the four elements.

Strontium. The concentration of strontium, which ranged from very low values up to about 1300 p.p.m. was observed to increase with increasing depths from which the water samples were obtained. The relationship of concentration to

sub-sea depth is illustrated in Fig. 4. Most of the points of Fig. 4 fall along a straight line, with certain exceptions. The point representing sample no. 102 lies below the curve, indicating an unexpectedly low concentration for the depth. This sample, which was obtained from a well in the southern part of the basin, an area presumably subjected to downwarping, is also anomalous in being of abnormally low salinity. The points representing sample nos. 31, 36 and 39 lie well above the curve, so that the strontium concentrations in these samples may be considered as

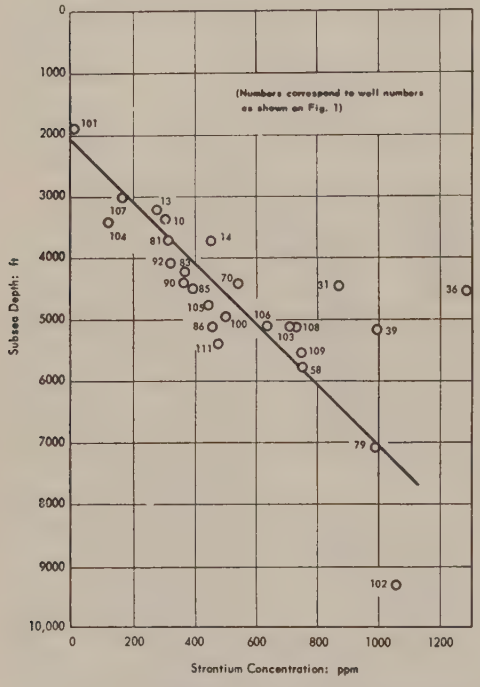


Fig. 4. Strontium content of Woodbine waters, East Texas area.

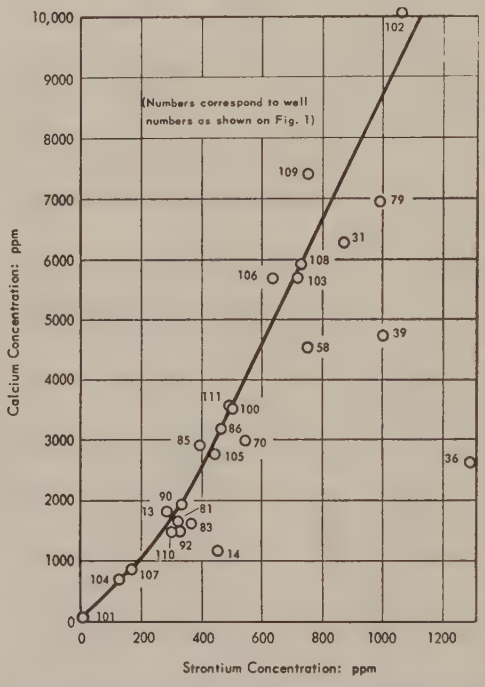


Fig. 5. Strontium and calcium concentrations of Woodbine waters, East Texas area.

being relatively high for their depths. It is interesting that the wells from which sample nos. 36 and 39 were secured are in close proximity to known salt domes. Whether or not there is a causal relationship is problematical, since the salinities of the waters from these two wells were essentially normal for the sampling depths.

Strontium concentrations and calcium concentrations (the latter determined some years ago) were found to be covariant. Fig. 5 shows the relationship between the two. Most of the points of Fig. 5, with the exception of points for sample nos. 36 and 39, fall close to the line drawn through them. Generally, Fig. 5 indicates the ratio of calcium concentration to strontium concentration to be in the range of 5–10 to 1. The calcium concentrations were determined by the calcium oxalate precipitation–potassium permanganate titration method. This method does not differentiate between dissolved calcium and strontium. Because of this the actual Ca : Sr concentration ratio is possibly lower than indicated by Fig. 5.

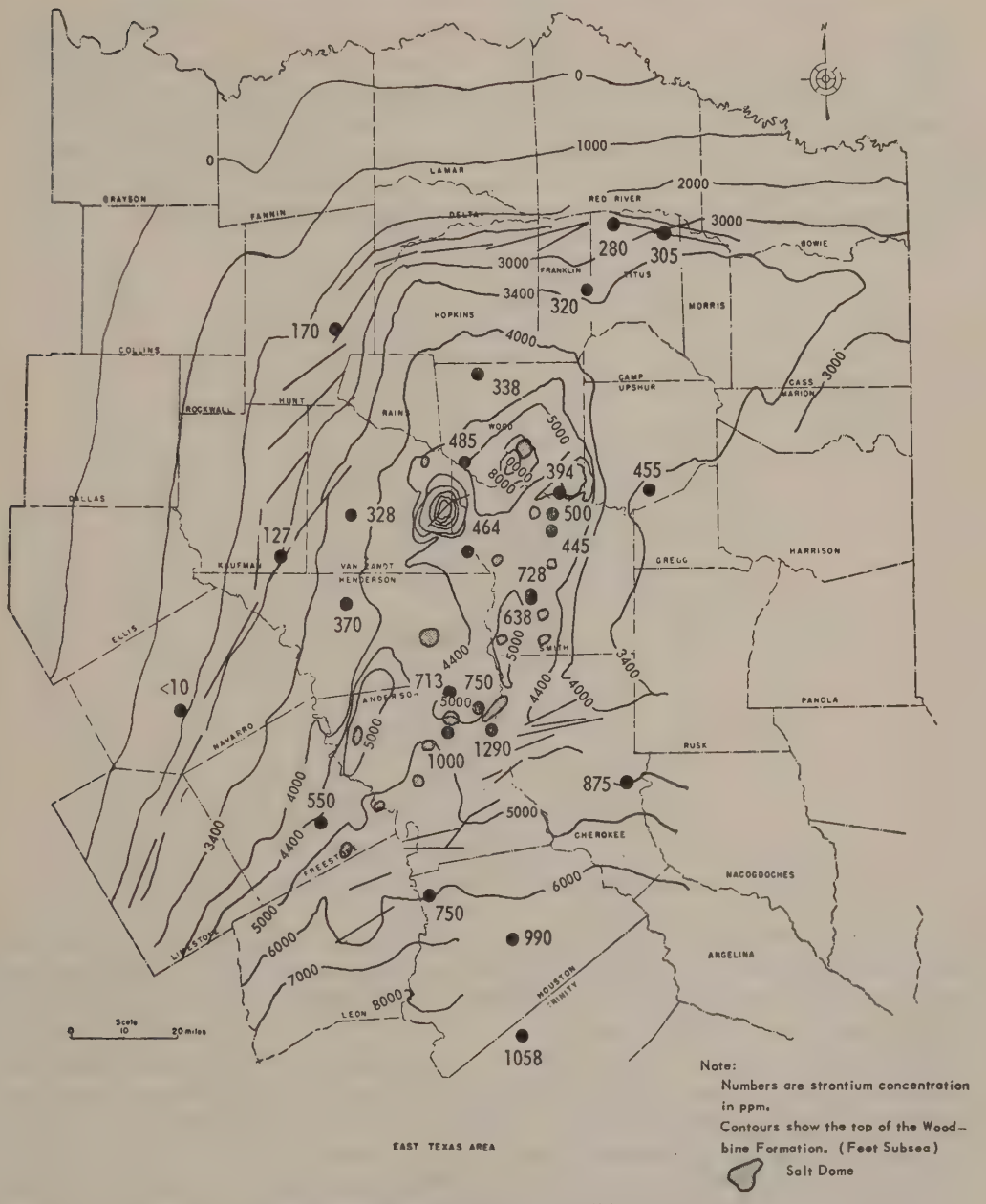


Fig. 6. Strontium content of Woodbine waters.

Also noted was a covariance of strontium and of magnesium concentrations, with the two elements present in approximately equal concentrations by weight.

There appears to be no relationship of strontium concentration to position within the basin, other than the general relationship of concentration to sampling depth. Fig. 6 is a map of the area showing the strontium values for each sample, and contours on top of the Woodbine sand.

Potassium. The concentration of potassium in the waters which were examined ranged up to about 350 p.p.m. From Fig. 7, which is a plot of potassium concentration versus sampling depth, it is apparent that there is a general trend of increasing concentration with increasing depth. The correlation, however, is not as good as that between depth and salinity (Fig. 2) or as that between depth and strontium concentration (Fig. 4). As in the case of strontium, what appear to be anomalously high concentrations of potassium were observed in sample nos. 31 and 36. Although

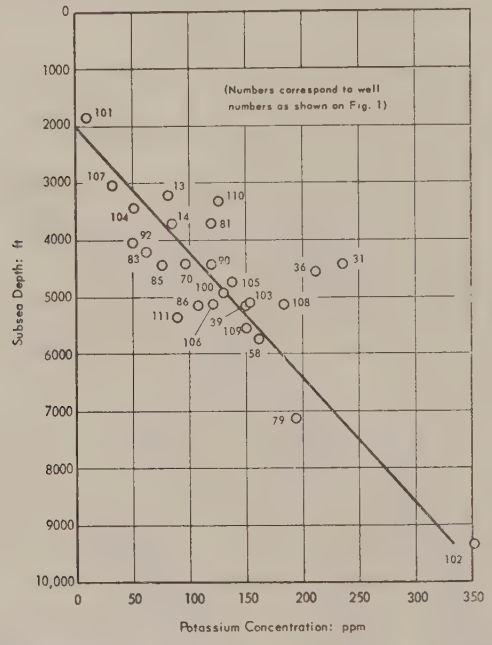


Fig. 7. Potassium content of Woodbine waters, East Texas area.

it might be supposed that the potassium concentration in the latter sample might have been influenced by proximity of the well to a salt dome, the potassium concentration in sample no. 39, which came from a well very close to a salt dome, exhibited no apparent abnormality.

Except for the trend of increasing potassium concentration with increasing depth, there was no observable relationship of potassium content to position within the basin. Fig. 8 presents potassium concentration plotted on the areal map, which also shows the depths of the top of the Woodbine sand.

Barium. The concentration of soluble barium was found to vary from very low values up to more than 50 p.p.m. Concentrations of the latter magnitude are surprisingly high, since all Woodbine waters contain at least traces of sulphate, and since barium sulphate has very low solubility. The solubility of barium sulphate is so low that in distilled water the barium content of a saturated solution is of the order of 1 p.p.m. Although the solubility of barium sulphate is known to increase with increasing salinity of the solution with which it is in contact, an examination of the data on barium content of Woodbine waters shows that the solubility must

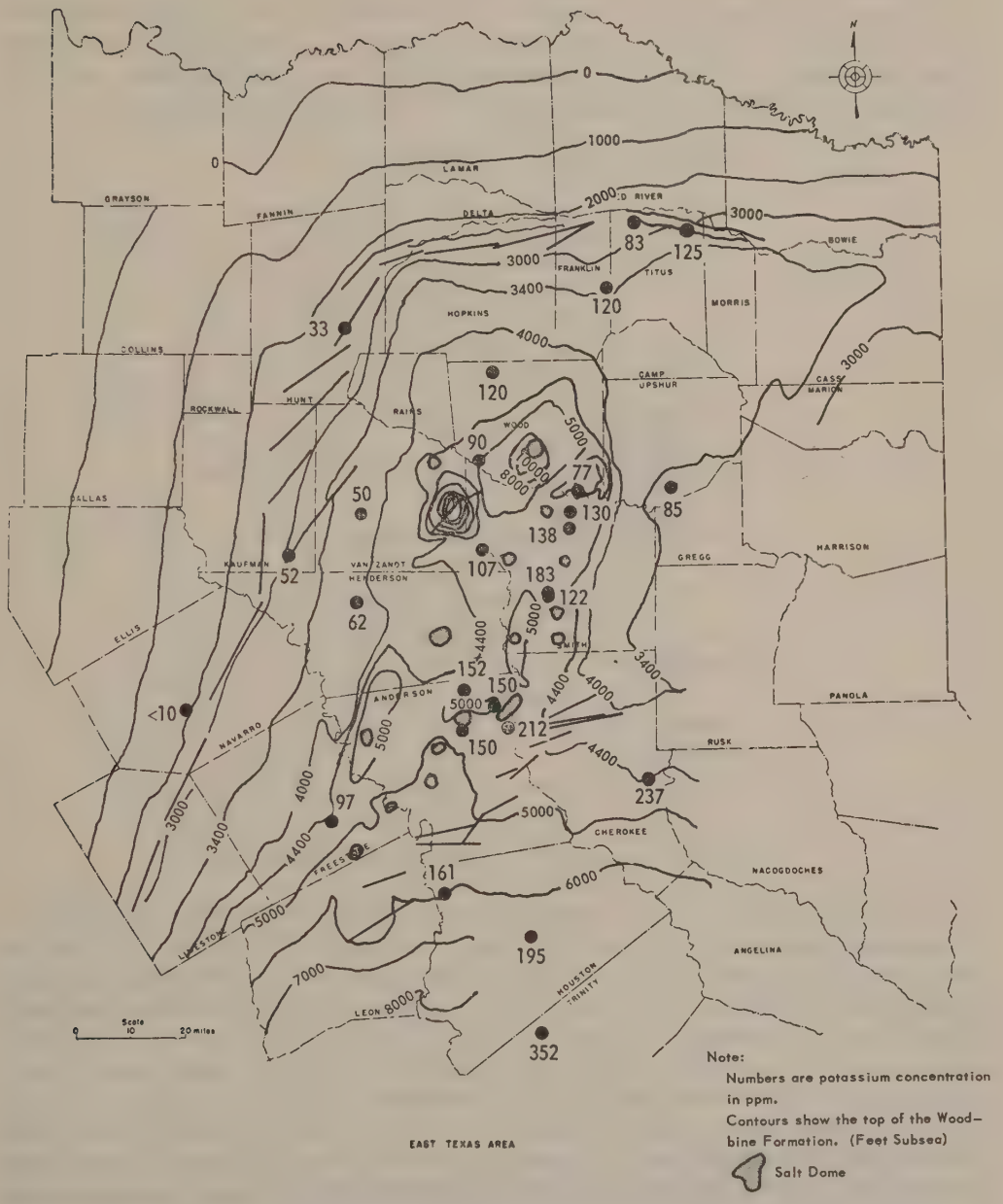


Fig. 8. Potassium content of Woodbine waters.

be increased by more than twentyfold to account for the barium concentrations observed in certain of the Woodbine samples.

As shown by Fig. 9, in which barium concentration is plotted against the depth from which sub-surface water was produced, there is no recognizable relationship of concentration to depth. The concentration is thus not covariant with the concentration of either of the alkaline earths, calcium and strontium.

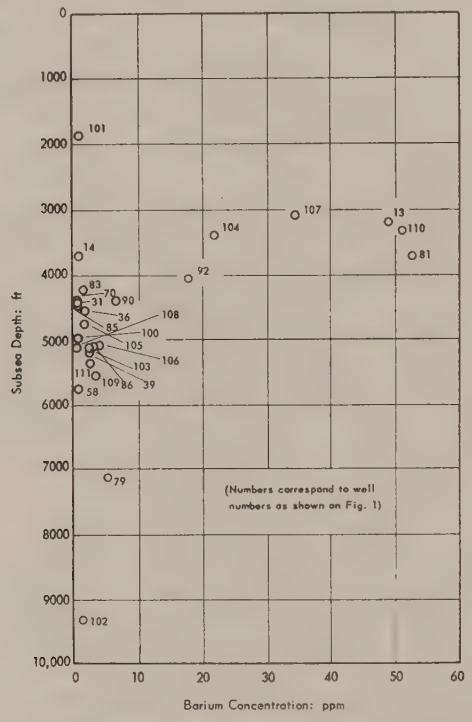


Fig. 9. Barium content of Woodbine waters, East Texas area.

The concentration of dissolved barium in Woodbine sub-surface waters shows a remarkable dependence on sampling location in the East Texas area. It may be seen from Fig. 10 that relatively high concentrations of dissolved barium were found in samples taken from wells on the northern and north-western periphery of the East Texas basin. Samples taken from wells in other parts of the basin contain only very low concentrations of dissolved barium. A possible exception is sample number 79, which came from the southern part of the basin, and which contained a moderate amount of barium.

According to the ideas expressed by Levinson (1955), the area in which high barium concentrations were found was essentially a shelf during one interval of Woodbine time. Levinson has postulated that the Woodbine sand was deposited in a shallow sea into which southward flowing rivers emptied. These rivers may have carried considerable quantities of dissolved barium salts, since their watersheds probably included the Cambrian barium sulphate deposits of Missouri and the deposits of Devonian to Pennsylvanian age of Arkansas. If barium were introduced

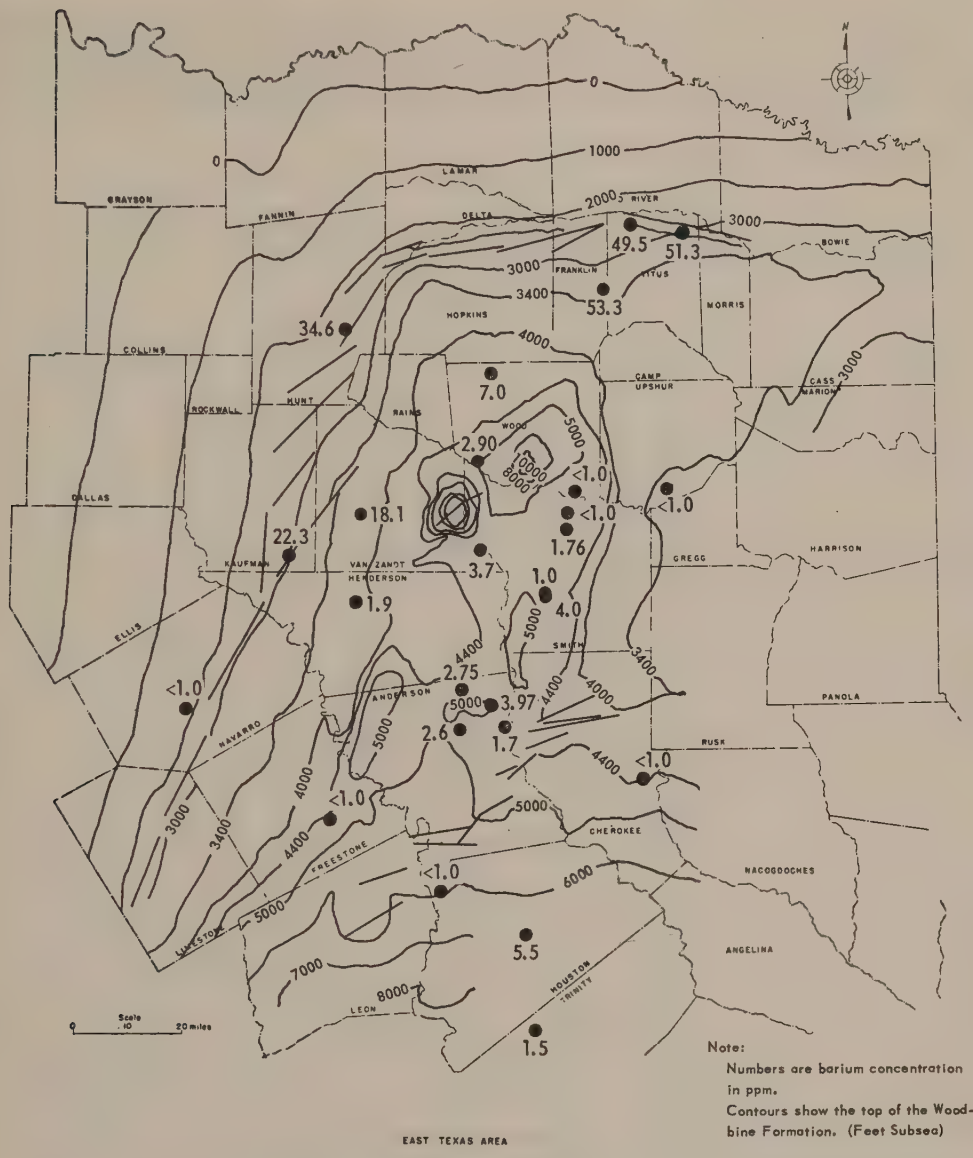


Fig. 10. Barium content of Woodbine waters.

into the Woodbine sea by the rivers, it is possible that it was concentrated in the shelf area by adsorption. If this be so, then subsequent desorption must be called upon to account for the presence of the relatively high barium concentration in the sub-surface waters of the northern and north-western parts of the basin. Although the events which produced high barium concentrations are by no means clear, it seems likely that the pattern of barium occurrence in the waters is a reflection of the depositional environment of the shelf area at a particular time in the evolution of the Woodbine basin.

Manganese. Manganese was found to occur in the sub-surface water samples in concentrations up to about 8 p.p.m. The variation of manganese concentration with depth is illustrated in Fig. 11. Although this figure indicates a general trend

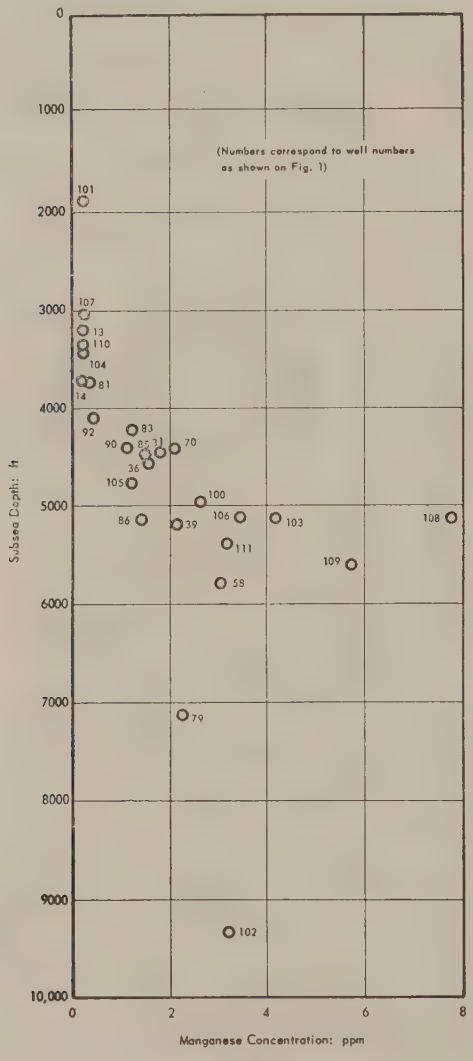


Fig. 11. Manganese content of Woodbine waters, East Texas area.

of increasing manganese concentration with increasing depth, the correlation is not nearly as good as that of salinity with depth, and the correlation becomes almost nonexistent at depths greater than about 5500 feet and at manganese concentrations in excess of about 3 p.p.m.

The pattern of manganese distribution within the basin is illustrated in Fig. 12, in which the contour lines depict the top of the Woodbine sand. There is a very striking dependence of manganese concentration on position within the basin.

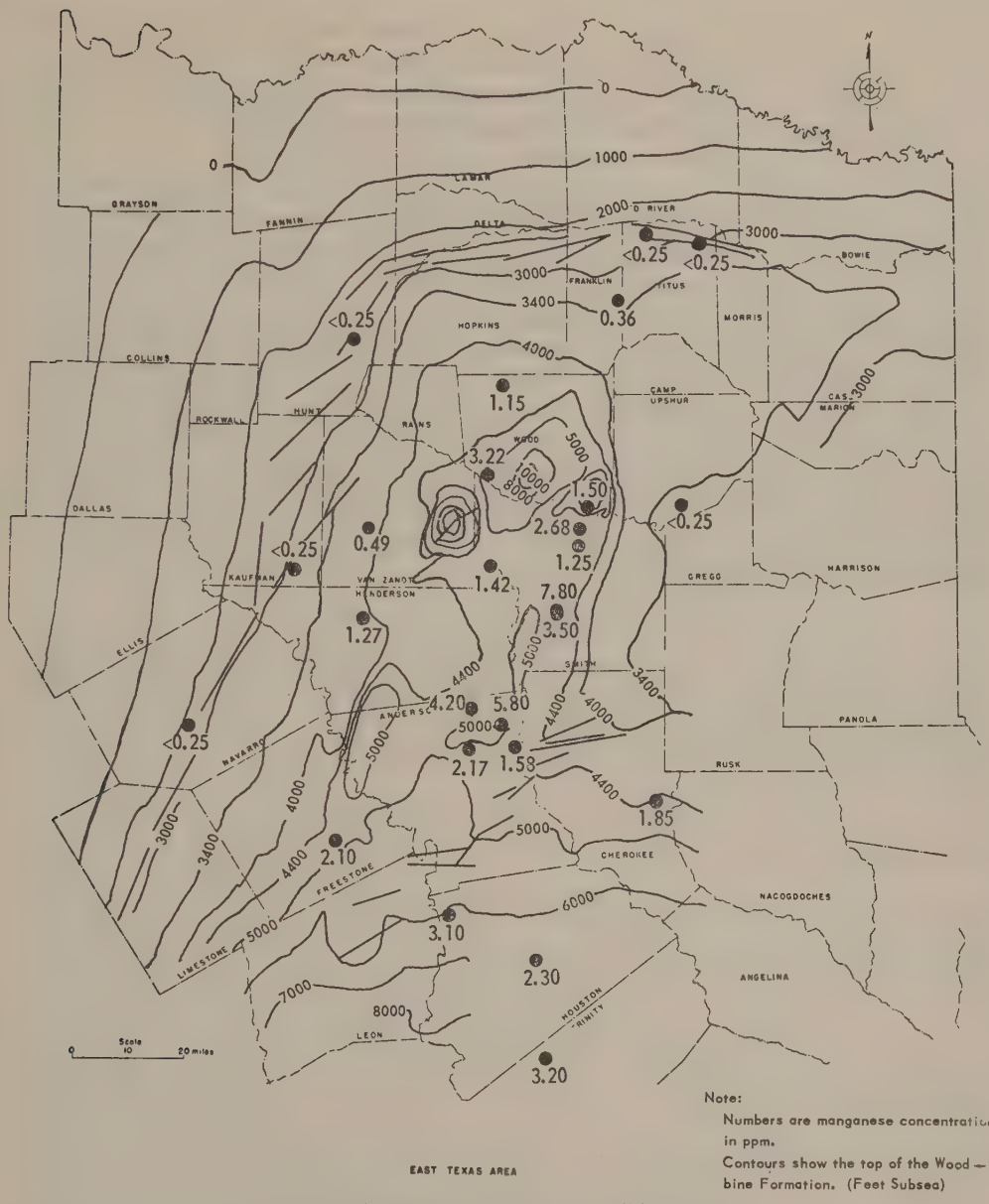


Fig. 12. Manganese content of Woodbine waters.

The concentrations around the periphery are uniformly low, and those in the central part are generally high. It is particularly interesting that only moderately high manganese concentrations are found in the southern part of the basin, which has apparently been downwarped. Except in the latter area, manganese is apparently concentrated in the deeper parts of the basin.

Manganese is unique among the elements in that it is a very sensitive indicator of the oxidizing or reducing conditions prevailing in any sedimentary environment

in which it may occur. Under oxidizing conditions (and in the absence of high acidity), the extremely insoluble manganese dioxide is formed, and the concentration of manganese in solution must necessarily be low. Under reducing conditions, however, manganese may be present in relatively soluble compounds, and the concentration of manganese in solution may be relatively high. In view of this behaviour of manganese, it is logical to suppose that its comparatively high concentrations in the deeper parts of the Woodbine basin are indicative of reducing conditions having prevailed there during the past. The lithology of the Woodbine sand, which is commonly a pink ferruginous sandstone, and of associated Woodbine shale, which is often reddish in color, suggests an oxidizing environment during deposition. It is entirely possible that the environment was indeed one in which oxidizing conditions were prevalent during deposition of the Woodbine member, and that reducing conditions did not appear until later. In this connection, it should be noted that the water which occurs in the Woodbine today is not necessarily connate—it could have had its origin in underlying or overlying beds, and could have pervaded the Woodbine during compaction of sediments. It is accordingly possible that reducing conditions could have ensued as a result of invasion of reducing waters from other strata.

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Beitrag zur Geochemie des Chroms

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Abstract—Chromium has been determined in 227 rocks and minerals by means of the diphenylcarbazide colorimetric method, which was modified for this purpose. The mean error of the method, expressed as the difference between duplicate determinations, is ±2%, and chromium contents down to 1 p.p.m. can be measured.

The analyses show that chromium is concentrated in the basic and ultrabasic rocks, while the granites investigated generally contained only about 1 p.p.m. Cr. In the basic rocks, the chromium is present in specific chromium minerals such as chromite and picotite, and also in magnetites and pyroxenes. The felspar contains almost no chromium.

The chromium content of volcanic rocks decreases steadily with increasing SiO_2 content. Thus, the melilite basalt of Gotzenbruhl with 34·7% SiO_2 contains 1380 p.p.m. Cr, while the Aar granite with 77% SiO_2 contains but 1 p.p.m. Cr.

Among the sedimentary rocks, high chromium contents are found in bauxites and in sedimentary iron ore deposits. In the bauxites this is due to relative (secondary) enrichment of chromium, while in the iron ores chromium may be associated with the iron in a colloidal state.

Pelitic sediments show a very uniform chromium content. Of 40 samples investigated, 24 contained between 70 and 110 p.p.m. Cr., while the remainder were also fairly close to these values.

For the most part, the chromium in sediments is concentrated in the micas and clay minerals, particularly in illite.

Zusammenfassung—Nach der kolorimetrischen Methode mit Diphenylcarbazid, die für diesen Zweck modifiziert wurde, sind an 227 Gesteinen und Mineralen Chrombestimmungen durchgeführt worden. Der mittlere Fehler der Methode, mit der man Chrommengen bis zu 1 p.p.m. nachweisen kann, beträgt bei je zwei Bestimmungen ±2%.

Die Analysen zeigen, dass das Chrom in den basischen und ultrabasischen Gesteinen angereichert ist, während die untersuchten Granite gewöhnlich nur 1 p.p.m. Cr enthielten. In den basischen Gesteinen steckt das Chrom in eigenen Chrommineralen, wie Chromit und Picotit, in den Magnetiten und in den Pyroxenen. Der Feldspat enthält fast kein Chrom.

Der Chromgehalt der Eruptivgesteine nimmt mit steigendem SiO_2-Gehalt kontinuierlich ab. So enthält der Melilithbasalt von Götzenbrühl 34,7% SiO_2 und 1380 p.p.m. Cr, der Aaregranit 77% SiO_2 und dementsprechend nur 1 p.p.m. Cr.

Bei den Sedimenten findet man hohe Chromgehalte in den Bauxiten und auch in manchen sedimentären Eisenerzlagerstätten. In den Bauxiten handelt es sich um eine relative Anreicherung des Chroms, in die Eisenerzlagerstätten kann es kolloidal mit dem Eisen gelangen.

Einen sehr gleichmässigen Chromgehalt weisen die Pelite auf. Von 40 untersuchten Proben liegen 24 zwischen 70 und 110 p.p.m. Die restlichen Proben liegen nahe um diese Werte herum.

Das Chrom der Sedimente steckt zum allergrössten Teil in den Glimmern und Tonmineralen und da vor allem im Illit. Die Mobilität des Chroms bei der Metamorphose ist sehr gering. Deshalb kann man mit Hilfe des Chromgehalts in manchen Fällen entscheiden, ob ein bestimmter Amphibolit ein Ortho- oder ein Paragestein ist.

Der durchschnittliche Chromgehalt für die Sedimente wurde zu 92 p.p.m. Cr berechnet. Der Chromgehalt der Eruptivgesteine konnte nicht genau berechnet werden. Es wurde angenommen, dass er nicht allzusehr vom mittleren Chromgehalt der Sedimente abweicht, so dass sich ein mittlere Chromgehalt der Erdruste von etwa 90 p.p.m. Cr ergibt.

Einleitung

Die erste Aufgabe der Geochemie ist es festzustellen, in welcher Menge die einzelnen Elemente in der Erdkruste vorkommen. Danach ist es wichtig und interessant zu untersuchen, welchen Weg das Element bei der Kristallisation aus dem Magma nimmt und wie es sich bei der Verwitterung und Metamorphose verhält. Dementsprechend beschäftigt sich die vorliegende Arbeit mit drei Fragen:

(1) Wie verteilt sich das Chrom auf die Eruptivgesteine und deren Minerale?

(2) Welchen Gang nimmt das Chrom bei der Verwitterung und Sedimentbildung?

(3) Kann man durch die Feststellung des Chromgehalts etwas über die Herkunft metamorpher Gesteine aussagen?

Methode

Die in der Einleitung gestellten Fragen lassen sich nur dann zufriedenstellend beantworten, wenn die Analysenergebnisse genau und zuverlässig sind. Da die spektralanalytische Untersuchung einen Fehler von etwa $\pm 10\%$ aufweist und bei geringen Chromgehalten nur noch Schätzungen zulässt, wurde zur Durchführung dieser Arbeit eine genauere kolorimetrische Methode entwickelt, die nun in kurzen Sätzen beschrieben werden soll. Mit Diphenylcarbazid als Reagens kann man Gehalte bis zu 1 μg Cr/l. nachweisen. Das Chrom muss zur Bestimmung als Cr^{VI} in schwach saurer Lösung vorliegen. Das in einer Achatschale feingepulverte Gestein wird durch eine Natriumperoxydschmelze aufgeschlossen, und zwar in Sinterkorundtiegeln. Das H_2O_2, das sich beim Auslaugen des Aufschlusses mit Wasser bildet, wird durch zweistündiges Behandeln auf dem Wasserbad soweit wie möglich entfernt. Das Eisen, das in stark alkalischer Lösung nicht ausfällt, wird durch einen Kationenaustauscher entfernt. Das Vanadium stört nur, wenn das Verhältnis V/Cr = 10/1 überschritten wird. Der relative Fehler der Methode aus zwei Einzelmessungen beträgt bei 100 μg Cr $\pm 2\%$. Unterhalb von 20 μg vergrössert sich der Fehler rasch und Werte unter 3 μg Cr bezeichnen nur noch eine Grössenordnung (Fröhlich, 1959).

Die Verteilung des Chroms in den Eruptivgesteinen

Es ist bekannt, dass sich das Chrom in den basischen und vor allem in den ultrabasischen Gesteinen anreichert, während die sauren Eruptivgesteine kaum Chrom enthalten. Goldschmidt (1954) stellte eine Tabelle auf, die auch nach den Ergebnissen dieser Arbeit gültig bleibt und die deshalb an dieser Stelle aufgeführt werden soll. Es ist selbstverständlich, dass die Werte dieser Tabelle nur als grössenordnungsmässige Angabe zu verstehen sind.

Gestein	Chromgehalt
Peridotit	3400 p.p.m. Cr
Gabbro	340 p.p.m. Cr
Diorit	68 p.p.m. Cr
Granit	2 p.p.m. Cr
Nephelin–Syenit	0,7 p.p.m. Cr

Chromgehalt der Minerale eines Eruptivgesteins

Wenn man die Geochemie eines Elementes be schreiben will, ist es nötig, ein Gestein in seine Minerale zu zerlegen und nachzuschauen, in welchen Mineralen sich ein Element anreichert und wo es nur in Spuren vorkommt. Zu solchen Untersuchungen bietet sich der Granit seiner grossen Mineralkörner wegen geradezu an. Leider ist es nicht möglich, die Verteilung des Chroms in den Mineralen des Granits zu studieren, weil er im Ganzen zu wenig Chrom enthält. Deshalb wurde

ein Basalt ausgesucht, und zwar der vom Dransberg b. Göttingen, weil er relativ grobkörnig ist.

Dennoch ist es der Verwachsungen wegen schwer, ein solches Gestein in seine Bestandteile zu zerlegen. Man muss schon zufrieden sein, wenn man eine hohe Anreicherung der einzelnen Minerale erreicht.

Praktisch wurde die Trennung wie folgt durchgeführt: Der Basalt wurde in einem Backenbrecher zerstückelt und danach in einer Walzenmühle soweit zerkleinert, dass genügend Material von der Korngrösse vorhanden war, die zur weiteren Verarbeitung taugte. Dann wurden die einzelnen Fraktionen abgesiebt. Das Material mit einer Korngrösse von 60–105 μ wurde durch einen Magnetscheider geschickt. So konnten die Minerale, beziehungsweise Mineralgruppen, Pyroxen, Olivin + Erz, Feldspat und Magnetit aussortiert werden. Um eine brauchbare Reinheit dieser Minerale zu erzielen, durchlief jede einzelne Gruppe mindestens sechsmal die Apparatur.

Danach lagen die Minerale in der Reinheit vor, wie sie bei der Zerlegung des Basalts nur erreicht werden kann. Die Verunreinigung durch das Restgestein betrug nach einer Kornanalyse unter dem Mikroskop etwa 6%.

Diese Konzentrate der einzelnen Minerale wurden auf ihren Chromgehalt untersucht. Das daraus folgende Analysenergebnis ist nicht mit dem wahren Chromgehalt des zu untersuchenden Minerals identisch, da die Analysensubstanz 6% Verunreinigungen enthält. Deshalb muss der gemessene Wert korrigiert werden. Dazu errechnet man aus dem Analysenergebnis und dem prozentualen Anteil des untersuchten Minerals am Gestein den Chromgehalt des Restgesteins. Dadurch ermittelt man nicht den völlig richtigen Chromgehalt des Restgesteins, weil man das Analysenergebnis seiner Berechnung zugrunde legen muss. Doch dieser Fehler ist so klein, dass er vernachlässigt werden darf. Der wahre Chromgehalt eines Minerals wird dann nach folgender Formel berechnet:

$$\text{Wahrer Chromgeh.} = \frac{\text{Analysenergeb.} - 0{,}06 \times \text{Cr—Geh. d. Restgest.}}{0{,}94}$$

Zur Verdeutlichung soll an dieser Stelle der korrigierte Chromgehalt des Feldspats nach dieser Formel bestimmt werden.

Analysenergebnis: 37 p.p.m. Cr.
Prozentualer Anteil des Feldspats am Gestein: 45%.
Chromgehalt des Feldspats im Gestein: $37 \times 0{,}45 = 16{,}6$.
Chromgehalt des gesamten Basalts: 335 p.p.m.

$$\text{Chromgehalt des Restgesteins} = \frac{335 - 16{,}6}{0{,}55} = 580 \text{ p.p.m.}$$

$$\text{Wahrer Chromgehalt} = \frac{37 - (0{,}06 \times 580)}{0{,}94} = 2 \text{ p.p.m.}$$

Damit ist der Chromgehalt des Feldspats bestimmt. Ebenso wurde mit den anderen Mineralen verfahren. In der folgenden Tabelle liegt das Ergebnis vor. Wie diese Tabelle ergibt, sind die dunklen Gemengteile die Träger des Chroms, während der Feldspat nahezu kein Chrom enthält. Der Magnetit nimmt etwa

Minerale	Cr (gem) (p.p.m.)	Cr (kor) (p.p.m.)	Prozentualer Anteil Anteil des Minerals am Gestein (%)	Cr–Anteil des Minerals am Gestein (p.p.m.)
(1) Feldspat	37	2	45	1,0
(2) Magnetit	388	390	2	7,8
(3) Olivin + Erz	680	705	18	127,0
(4) Pyroxen	560	580	35	203,0
(5) Gesamtgest	335			338,8

soviel Chrom auf, wieviel das ihn umgebende Magma enthält. Es ist anzunehmen, dass die 390 p.p.m. Cr des Magnetits zum grössten Teil an Stelle des Eisens im Gitter eingebaut vorkommen.

Einen erstaunlich hohen Chromgehalt zeigt der Pyroxen, der damit zum wichtigsten Träger des Chroms im Gestein wird. Mit diesem einen Beispiel kann man noch nicht allzuviel anfangen. Man kann vor allem noch nicht sagen, dass der Pyroxen ganz allgemein das bedeutendste "Chrommineral" sei. Wenn man aber die Ergebnisse von de Vore (1955a,b) mit hinzuzieht, der in 17 Gesteinen die Pyroxene auf ihren Chromgehalt untersucht hat und Werte bis 5500 p.p.m. Cr findet, darf man behaupten, dass der Pyroxen ausserordentlich hohe und bedeutende Mengen von Chrom enthält. Wager und R. L. Mitchell (1951) finden in Pyroxenen basischer Eruptivgesteine bis zu 3000 p.p.m. Cr. Weiterhin kann in diesem Zusammenhang auf die Arbeiten von Nockolds und Mitchell (1948) Cornwall und Rose (1957), Snyder (1959) und N. Sen *et al.*, (1959) hingewiesen werden, die übereinstimmend hohe Chromgehalte in den Pyroxenen basischer Eruptivgesteine angeben.

Da der Pyroxen bei der Betrachtung des Chroms so wichtig ist, wurde geprüft, ob das Chrom im Gitter des Minerals eingebaut ist, oder ob es in Chromiteinsprenglingen vorliegt. In Streupräparaten wurde der Pyroxen unter dem Mikroskop auf Einschlüsse untersucht. Dabei wurden in 500 Körnern keine Chromit- und nur zwei Picotiteinschlüsse gefunden. Das spricht dafür, dass das Chrom im Gitter eingebaut vorliegt, denn diese wenigen Einschlüsse tragen nur unwesentlich zum Chromgehalt des Minerals bei.

Bei Probe (3), Olivin + Erz handelt es sich um ein Mineralgemisch, das nicht weiter getrennt werden konnte. Es enthält alle im Gestein vorkommenden Minerale ausser Pyroxen, Magnetit und Feldspat. Das wichtigste Chrommineral des Gemischs ist der Picotit.

Da es interessant ist festzustellen, ob der Olivin Chrom enthält und wieviel das etwa sein könnte, wurde eine Olivinknolle aus dem Basalt vom Hohen Hagen untersucht. Im Gegensatz zu Probe (3) lässt sich in der Knolle der Olivin von den übrigen Mineralen trennen. Sonst entspricht die Knolle weitgehend dem Mineralgemisch der Probe (3).

Zunächst wurde der Chromgehalt der gesamten Knolle untersucht und dabei

wurden 1010 p.p.m. gefunden. Die aus dieser Knolle aussortierten Olivine enthielten nur 100 p.p.m. Cr. Die grosse Zahl der Picotiteinsprenglinge im aussortierten Olivin lässt vermuten, dass—wenn überhaupt etwas—doch nur sehr wenig Chrom ins Gitter des Olivins eingebaut wird.

Nach dieser Untersuchung findet man drei Stellen, an denen sich das Chrom bei der Bildung eines Basalts ausscheidet:

(a) Es bilden sich eigene Chromminerale wie der Chromit und der Picotit.

(b) Das Chrom wird ins Gitter des Magnetits aufgenommen. Die Chromkonzentration ist im Magnetit nicht wesentlich höher als im umgebenden Gestein.

(c) Das Chrom wird ins Pyroxengitter eingebaut.

Die Olivinbasalte	(p.p.m. Cr)
(5) Olivinbasalt vom Dransberg b. Göttingen.	335
(6) Olivinbasalt vom Hohen Hagen b. Göttingen (Org. Mat. WEDEPOHL, 1950).	412
(7) Olivinbasalt vom Steinberg b. Barlissen.	418
(8) Trachydoleritischer Basalt, Backenberg b. Güntersen Südniedersachsen (Org. Mat. WEDEPOHL, 1954) Probe (1).	305
(9) Dasselbe Gestein, Probe (5).	282
(10) Dasselbe Gestein, Probe (4).	276
(11) Trachydoleritischer Basalt, Gahrenberg, Reinhardswald, Bruch der Forstverwaltung.	258
(12) Olivinbasalt, untere Bramburg b. Göttingen.	254
Tholeyitische Basalte	(p.p.m. Cr)
(13) Basalt v. Chakula, Zentral-Indien (Org. Mat. v. ENGELHARDT, 1936, Probe: 2092).	35
(14) Basalt v. Linga, Zentral-Indien (Org. Mat. v. ENGELHARDT, 1936, Probe: 1156).	39
(15) Basalt v. Shikarpur, Zentral-Indien (Org. Mat. v. ENGELHARDT, 1936, Probe: 1158).	79
(16) Basalt v. Shikarpur, Zentral-Indien (Org. Mat. v. ENGELHARDT, 1936, Probe: 1153).	79
(17) Durchschnitt von 9 Basalten, z. T. aus Basaltströmen, Zentral-Indien (Zusammensetzung s. v. ENGELHARDT, 1936).	67
(18) Gangbasalt, Centerville, Fairfax County, Virginia, (U.S. Geol. Survey, Standardprobe W 1).	125
Melilithbasalte	(p.p.m. Cr)
(19) Melilithbasalt, Westberg b. Hofgeismar.	670
(20) Melilithbasalt, Hochbohl, Schwäb. Alb.	1170
(21) Melilithbasalt, Götzenbrühl, Schwäb. Alb.	1380
Restliche basaltische Gesteine	(p.p.m. Cr)
(22) Foid-Basalt, Druseltal b. Kassel.	264
(23) Basalttuff, Ahrensberg, westl. Habichtswald.	350
(24) Lapilli-Schlacke, Bausenberg b. Niederzissen.	190
(25) Mischung aus 11 deutschen Gabbros (Zusammensetzung s. NOLL, 1934).	365
(26) Gabbro, Oberhalbstein, Graubünden.	20
(27) Gabbro, Radautal b. Harzburg im Harz.	160
(28) Pyroxen aus dem Gabbro vom Radautal.	334

Basalte

Es wurde 23 basaltische Gesteine auf ihren Chromgehalt untersucht und zwar 8 Olivinbasalte, 6 tholeyitische Basalte, 3 Melilithbasalte und ausserdem noch 6 basaltische Gesteine verschiedener Herkunft und Zusammensetzung. Beim Vergleich der drei hier untersuchten Basalttypen, des Olivinbasalts, des tholeyitischen Basalts und des Melilithbasalts fällt auf, dass die Chromgehalte innerhalb der einzelnen Typen sehr ähnlich sind, dass sich aber die drei Basalttypen untereinander deutlich unterscheiden. Der Melilithbasalt, ein abnormes basaltisches Gestein, zeichnet sich durch besonders hohe Chromwerte aus.

Die Olivinbasalte aus der Umgebung von Göttingen ähneln sich nicht nur in ihrem Chromgehalt, sondern auch in ihrem Gehalt an SiO_2. Dabei ist es auffällig, dass sich schon geringe Änderungen des SiO_2-Gehalts in den Chromwerten widerspiegeln. Das beste Beispiel dazu liefern die drei Proben des trachydoleritischen Basalts vom Backenberg b. Güntersen in der Nähe von Göttingen. Die SiO_2-Werte

	(p.p.m. Cr)	(% SiO_2)
(8) Probe (1)	305	48,6
(9) Probe (5)	282	49,2
(10) Probe (4)	276	50,0

sind der Arbeit von K. H. Wedepohl (1954) entnommen. Diese hier festgestellte Abhängigkeit kann durchaus als zufällig angesehen werden. Wenn man aber bedenkt, dass auch der Basalt vom Hohen Hagen mit einem Chromgehalt von 412 p.p.m. und einem SiO_2-Gehalt von 47,8% dazu passt, und dass stets eine Abnahme des Chroms von den basischen zu den sauren Gesteinen festgestellt wird, ist man geneigt, die Beziehungen zwischen dem Chrom- und dem SiO_2-Gehalt beim Basalt vom Backenberg nicht für zufällig zu halten.

Die Melilithbasalte passen mit ihrem hohen Chrom- und niedrigen SiO_2-Gehalt sehr gut zu dem, was bei den Göttinger Basalten festgestellt wurde. Mit sinkendem SiO_2-Gehalt nimmt der Chromgehalt der Melilithbasalte zu. Die genauen Verhältnisse werden im Zusammenhang mit allen Eruptivgesteinen am Schluss des Kapitels in einer Tabelle dargestellt.

Nun soll untersucht werden, in welchem Mineral des Melilithbasalts das Chrom steckt. Dazu eignet sich der Melilithbasalt vom Westberg b. Hofgeismar, der von Th. Ernst (1936) petrographisch untersucht worden ist. Nach seinen Angaben besteht das Gestein zu 40% aus Mineralen, die sich auch in den Knollen finden, und darin findet er 0,9% Picotit. Das ergibt einen Picotitgehalt von 0,36% für das gesamte Gestein. Der Picotit enthält nach seinen Angaben 22,83% Cr_2O_3 oder 15,65% Cr. Demnach sind 563 p.p.m. Cr im Picotit gebunden. Da der gesamte Melilithbasalt vom Westberg nur 670 p.p.m. Cr enthält, darf man folgern, dass der wesentliche Teil des Chroms bei diesem Basalt in eigenen Mineralen kristallisiert.

Dieser etwas umständliche und nicht sehr genaue Weg über die Berechnung musste beschritten werden, da es nicht möglich war, den Picotit von den anderen Mineralen abzutrennen.

Der hohe Chromgehalt des Melilithbasalts vom Westberg wie der Melilithbasalte

von Hochbohl und Götzenbrühl aus der schwäbischen Alb, die von G. Leopold (1940) petrographisch bearbeitet wurden, ist deshalb so interessant, weil er darauf hinweist, dass es sich bei den Melilithbasalten um Reaktionsprodukte mit frühmagmatischen Ausscheidungen handelt.

Um festzustellen, ob auch im Gabbro wie im Basalt vom Dransberg der Pyroxen der wichtigste Träger des Chroms ist, wurde der Pyroxen aus dem Gabbro vom Radautal abgetrennt und analysiert. Dabei wurden 334 p.p.m. Cr gefunden. Da der Gabbro des Radautals nach Dünnschliffuntersuchungen zu 42% aus Pyroxen besteht, berechnet man 140 p.p.m. Cr im Pyroxen. Die restlichen Minerale enthalten dann insgesamt nur noch 20 p.p.m. Cr. Damit erweist sich der Pyroxen auch im Gabbro als der wichtigste Träger des Chroms. –Der Olivin–Nephelinit

Diorite und Andesite	(p.p.m. Cr)
(29) Durchschnitt von 14 Andesiten, Methana (Halbinsel im Saronischen Golf, Griechenland) (Zusammensetzung s. v. Engelhardt, 1936).	50
(30) Quarz–Glimmer–Diorit, Rossbach, Bayrischer Wald.	44
(31) Quarz–Diorit, (Tonalit), Adamello, Südtirol.	11
(32) Augit–Andesit, Tokay, Ungarn.	20
(33) Pyroxen–Andesit, Forstbruch, Sababurg, Reinhardswald.	136
(34) Porphyrit–(Andesit), Mathias–Schmidt–Berg, Harz.	200
Tephrite und Nephelinite	(p.p.m. Cr)
(35) Leuzit–Nephelin–Tephrit, Ettringer Bellerberg, Eifel.	82
(36) Leuzit–Nephelin–Tephrit, Niedermendig, Laacher See.	25
(37) Olivin–Nepelinit, Mühlenberg b. Hohenfels, Steinbruch Zettelmayer, Eifel.	115

zeigt unter den Tephriten und Nepheliniten den höchsten Chromgehalt. Da bei den beiden häufigsten Basalttypen, den tholeyitischen und den Olivin–Basalten, auch die Olivinbasalte die höheren Chromwerte aufweisen—die in dieser Arbeit untersuchten tholeyitischen Basalte haben im Durchschnitt weniger als 100 p.p.m. Cr, während die Olivinbasalte bei durchschnittlich 300 p.p.m. Cr liegen—könnte man vermuten, mit zunehmendem Olivin würden auch die Chromgehalte der Eruptivgesteine steigen. Eine Prüfung ergab jedoch, dass eine einfache Abhängigkeit zwischen beiden nicht nachzuweisen ist. Nur das kann mit Sicherheit gesagt werden, dass olivinhaltige basische Gesteine im allgemeinen mehr Chrom enthalten als olivinfreie. –Die Gruppe der hier aufgeführten Gesteine enthält nur sehr wenig Chrom. Das einzige Gestein, das dabei etwas aus dem Rahmen fällt, ist der Syenit von Zitschewig. Um festzustellen, ob der hohe Chromgehalt des Syenits von Zitschewig etwa durch Verunreinigungen bei der Herstellung der Probe entstanden ist, wurde nicht nur die vorliegende, schon gemahlene Probe der geochemischen Sammlung untersucht. Es wurde ausserdem noch festes Gestein in der Achatschale zerkleinert und analysiert. Diese Analyse ergab 39 p.p.m. Cr, also praktisch das gleiche Ergebnis. Damit ist erwiesen, dass der Syenit von Zitschewig Chrom in deutlicher Menge enthält. Hohe Chromwerte für Syenite findet auch Sahama (1945)

Syenite, Nephelinsyenite, Trachyte und Phonolithe	(p.p.m. Cr)
(38) Durchschnitt von 22 Nephelinsyeniten (Zusammensetzung s. v. Engelhardt, 1936).	1
(39) Syenit, Zitschewig b. Dresden.	42
(40) Trachyt, Drachenfels, Siebegebirge, Rheinland.	1
(41) Trachyt, Wölferlingen b. Freilingen, Westerwald.	1
(42) Durchschnitt von 10 deutschen Phonolithen (Zusammensetzung s. v. Engelhardt, 1936).	5
(43) Durchschnitt von 14 böhmischen Phonolithen (Zusammensetzung s. v. Engelhardt, 1936).	4
(44) Noseanphonolith, Kempenich, Eifel.	1
(45) Noseanphonolith, Schellkopf b. Brenk, Eifel.	1
(46) Laudarlith, Larvik, Norwegen.	1

bei der Untersuchung des Basement Complex in Südlappland. Er gibt als Durchschnittswert für die dortigen Syenite 200 p.p.m. Cr an. Siebzehn Granite sind

Granite und Liparite	(p.p.m. Cr)
(47) Rönne–Granit, Bornholm.	1
(48) Vang–Granit, Bornholm.	1
(49) Hammer–Granit, Bornholm.	1
(50) Gudhjem–Granit, Bornholm.	1
(51) Durchschnitt von 14 deutschen Graniten (Zusammensetzung s. Noll, 1934).	32
(52) Granit, Andlau, Nord, Nordvogesen.	10
(53) Granit, Andlau, Süd, Nordvogesen.	6
(54) Aare–Granit, Gurtnellen, Kanton Uri, Schweiz.	1
(55) Granit vom Brockenmassiv, Schierke, Harz.	1
(56) Granit, dasselbe Wurmberg, Harz (Org. Mat. Niemann, 1958) Probe (1).	1
(57) Dasselbe Gestein, Probe (3).	1
(58) Dasselbe Gestein, Probe (5).	1
(59) Lithionit–Granit, Eibenstock, Sachsen.	1
(60) Granit, Eklara, Indien (Originalprobe 105 von Köster, 1955).	2
(61) Granit, Westerly, Rhode Island (U.S. Geol. Survey Washington, Standardprobe G 1) (Fairbairn, 1951).	20
(62) Liparit, Island (Originalprobe L 1, Sigvaldason, 1958).	1
(63) Liparit, Island (Originalprobe L 2, Sigvaldason, 1958).	1

untersucht worden, und nur bei vier Proben liegt der Chromgehalt deutlich über 1 p.p.m. Es ist erstaunlich, dass so viele Proben gleich wenig Chrom enthalten, während vier Proben sich zum Teil stark davon unterscheiden. Das merkwürdigste dabei ist aber, dass gerade die Durchschnittsmischung den höchsten Chromgehalt aufweist. Man sollte doch annehmen, diese Mischung würde wenigstens so einigermassen in der Mitte der anderen Werte liegen.

Für den übermässig hohen Chromgehalt der Mischung mag es zwei Gründe geben. Einmal darf man daran zweifeln, ob alle zu dieser Mischung verwandten

Gesteine eindeutig als Granite angesprochen werden dürfen. (Zur Herstellung der Durchschnittsmischung wurden von Noll Granite aus dem Odenwald, den Vogesen, dem Bayrischen Wald, dem Fichtelgebirge, dem Erzgebirge, aus Schlesien und aus Sachsen benutzt.) Zum anderen ist es nicht ausgeschlossen, dass durch die Stahlgeräte, mit denen die Granite zerkleinert worden sind, Chrom in die Probe gelangt ist. Deshalb wurde wie beim Syenit von Zitschewig eine neue Probe des Granits Andlau, Nord bereitet und untersucht. Diese Analyse ergab nicht 10 sondern nur 1 p.p.m. Cr. Die erstaunliche Diskrepanz in den beiden Analysen lässt vermuten, dass der Granit von Andlau nur 1 p.p.m. Cr enthält, während die 10 p.p.m. Cr, die in der Probe der geochemischen Sammlung gefunden wurden, aus Verunreinigungen stammen, die möglicherweise durch die Zerkleinerung mit Stahlgeräten entstanden sind. Es ist nicht ausgeschlossen, dass der gleiche Effekt für den hohen Chromgehalt der Durchschnittsmischung verantwortlich ist.

Da es nicht sicher ist, ob bei der Durchschnittsmischung der wirkliche Chromgehalt des Gesteins bestimmt worden ist, oder ob Verunreinigungen das Analysenergebnis verfälscht haben, soll diese Probe aus den weiteren Betrachtungen ausgeschlossen werden. Aus dem selben Grunde werden bei der folgenden Erörterung nur die Proben berücksichtigt, deren Feinzerkleinerung mit Sicherheit in einer Achatschale erfolgte. Das sind sämtliche Granite von Bornholm, der Aare–Granit, der Granit von Eklara, die Granite vom Wurmberg sowie die Liparite von Island.

Mit Erstaunen stellt man fest, dass alle diese Gesteine praktisch nicht mehr als 1 p.p.m. Cr enthalten. Wenn es erlaubt ist, aus diesen wenigen Proben schon einen Schluss zu ziehen, und wenn man weiter annimmt, dass die hier aufageführten Granite in der Mehrzahl durch Differentiation entstanden sind, darf man behaupten, dass im Laufe der Differentiation das gesamte Chrom des ursprünglichen Magmas in den Erstausscheidungen verbraucht wird, so dass das granitische Restmagma praktisch Chrom mehr enthält.

Um diese These zu stützen, wurden Granite untersucht, die extrem viel dunkle Gemengteile enthalten. Es sind die schon aufgeführten Granite von Rönne und Vang auf Bornholm. Der Rönne–Granit enthält nach Angabe von Callisen (1934) 10,0% Hornblende und 5,0% Biotit, der Vang–Granit 5,1% Hornblende und 6,2% Biotit. Der Erzgehalt der beiden Granite liegt bei 4%. Sen *et al.*, (1959) finden in 4 Graniten und Granodioriten, dass die Quarze und Feldspäte kein Chrom enthalten, dass dagegen die Biotite bis zu 80 p.p.m. Cr und die Hornblenden bis zu 90 p.p.m. Cr aufweisen. Wenn man demnach hohe Chromgehalte in Graniten finden will, dann muss man schon in biotit- und hornblendereichen Graniten nachsehen. Wenn aber schon die an dunklen Gemengteilen so reichen Granite von Rönne und Vang nicht mehr als 1 p.p.m. Cr enthalten, dann ist kaum zu erwarten, dass ein anderer aus der Differentiation des Magmas entstandener Granit einen wesentlich höheren Chromgehalt aufweisen wird.

Das Verhältnis Cr/SiO_2 *in den Eruptivgesteinen*

Wie schon bei der Betrachtung der Basalte aus der Umgebung von Göttingen erwähnt wurde, findet man in einem Eruptivgestein um so weniger Chrom, je mehr Kieselsäure es enthält. Nachdem nun auch die Analysen der sauren

Eruptivgesteine angegeben sind, ist es vielleicht ganz instruktiv, den Chromgehalt neben dem SiO_2–Gehalt, soweit er bekannt ist, in einer Tabelle aufzutragen.

Gestein	Cr (p.p.m.)	SiO_2 (%)
(54) Aare–Granit.	1	77,0
(55) Wurmberg–Granit.	1	73,3
(52) Andlau–Granit.	1	69,0
(31) Diorit, Adamello.	11	59,6
(30) Diorit, Rossbach.	44	52,0
(10) Basalt, Backenberg, Probe (4).	276	50,0
(9) Basalt, Backenberg, Probe (5).	282	49,2
(8) Basalt, Backenberg, Probe (1).	305	48,6
(6) Basalt, Hoher Hagen.	412	47,8
(19) Melilithbasalt, Westberg.	670	46,6
(20) Melilithbasalt, Hochbohl.	1170	36,6
(21) Melilithbasalt, Götzenbrühl.	1380	34,7

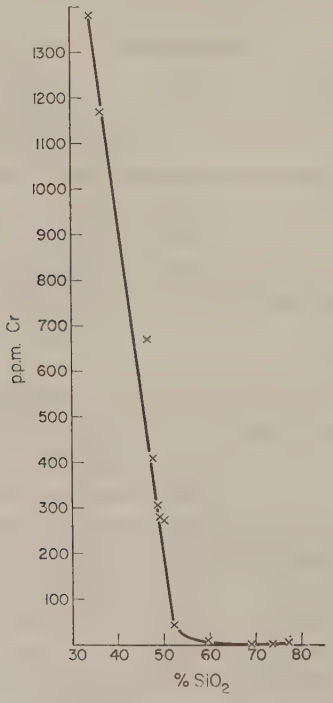

Abb. 1. Cr/SiO_2 Verhältnis in Eruptivgesteinen.

Das Chrom in den Sedimentgesteinen

Vor der Betrachtung der Sedimente ist es angebracht, das Verhalten des Chroms bei der Verwitterung von Eruptivgesteinen zu untersuchen. Denn da eröffnet sich eine gute Möglichkeit, die Mobilität des Chroms bei der Bildung von Sedimenten festzustellen.

Zwei Verwitterungsprofile über Granit

Bei dem ersten Verwitterungsprofil handelt es sich um das von KÖSTER (1955) bearbeitete indische Lateritprofil von Kot, Provinz Gujarat (Indien).

	(p.p.m. Cr)
(64) Probe (104), Ob. Konkretionshorizont, Konkretion.	152
(65) Probe (103), Heller Horizont, Ton.	165
(66) Probe (103), Heller Horizont, Konkretion.	165
(67) Probe (102), Unt. Konkretionshorizont, Ton.	82
(68) Probe (101), Kaolinisierter Granit, Ton.	23
(60) Probe (105), Granit von Eklara.	2

In seiner Arbeit schreibt KÖSTER über die Verwitterung des Granits von Eklara, den er an Stelle des unzugänglichen Granits von Kot als Ausgangssubstanz benutzt: "Der Granit bei Kot und Eklara ist einer Kaolinisierung unterworfen gewesen. Dabei wurden die Feldspäte und Hornblende vollständig zerstört. Die Quarzkörner wurden erheblich korrodiert, der Biotit gebleicht und teilweise abgebaut."

Wie bei der Betrachtung des Granits festgestellt wurde, ist das Chrom in der Hornblende und im Biotit zu suchen, während Quarz und Feldspat chromfrei sind. Ein Teil von den 2 p.p.m. Cr, die im Ausgangsgestein vorlagen, kann bei der Kaolinisierung des Granits in den unverwitterten Mineralen geblieben sein, zum Beispiel im gebleichten Biotit. Der grössere Teil wird aber mit dem abgebauten Biotit und der Hornblende aufgelöst worden sein. Da eine starke Anreicherung des Chroms im Profil festgestellt wird, ist anzunehmen, dass das gelöste Chrom nicht weggeführt worden ist, sondern gleich nach der Auflösung aus dem Mineral als Chromhydroxyd wieder ausfiel. So kann eine relative Anreicherung des Chroms im Profil stattgefunden haben. Dafür spricht vor allem die kontinuierliche Zunahme des Chroms mit steigender Verwitterung.

Einige Bedenken an dieser Erklärung entspringen der Tatsache, dass eine Anreicherung um den Faktor 165/2 = 82,5 stattgefunden hat. Es dürften, wenn man eine relative Anreicherung voraussetzt, in Probe (103) nur noch 1,17 % vom ursprünglichen Gestein übrig geblieben sein.

Eine endgültige Klärung der Frage, wie sich das Chrom in diesem Profil angereichert hat—ob es sich um eine relative Anreicherung handelt, oder ob man eine Zufuhr chromhaltiger Lösungen annehmen muss—wird sich erst ergeben, wenn die Arbeit von KÖSTER über die Verteilung der Spurenelemente in diesem Profil abgeschlossen ist.

Neben diesen allgemeinen Feststellungen fällt noch eine Kleinigkeit in dem Profil auf. Die Proben (65) und (66) enthalten gleich viel Chrom. Beide Proben sind aus dem selben Horizont. Die Konkretionen unterscheiden sich dadurch vom Ton, dass sie mehr Eisen enthalten. Nach KÖSTER sind die Konkretionen sekundäre Bildungen im Profil. Daraus kann man schliessen, dass das Chrom, das sich bei der Lateritbildung zusammen mit dem Eisen anreichert, bei der Entstehung der Eisenkonkretionen nicht mehr mobil war.

Das zweite Verwitterungsprofil, das auf Chrom untersucht wurde, ist von

Piller (1951) petrographisch untersucht worden. Es ist ein Profil über Granit aus der Nähe von St. Andreasberg im Harz.

	(p.p.m. Cr)
(69) Granit, Piller 16, stark verlehmt (30 cm Tiefe).	21
(70) Granit, Piller 15, beginnende Verlehmung (1 m Tiefe).	8
(71) Granit, Piller 17, in Grus zerfallen (2 m Tiefe).	6
(72) Granit, Piller 14, frischestes Gestein (5 m Tiefe).	7

Auch das frischeste Gestein war der Verwitterung schon ausgesetzt. So ist es verständlich, dass die Probe (72) einen höheren Chromgehalt zeigt als andere Harzgranite. Dieser Chromgehalt bleibt bis zu einer Tiefe von einem Meter nahzu gleich und steigt erst nahe der Erdoberfläche zu einem höheren Wert an. Im ganzen sieht man bei diesem Profil wie bei dem von Kot eine Zunahme des Chromgehalts mit fortschreitender Verwitterung.

Eine ähnliche Anreicherung des Chromgehalts im Laufe der Verwitterung finden Gordon und Murata (1952) in den Bauxiten von Arkansas. Das Ausgangsgestein dieser Bauxite ist ein Nephelinsyenit. In der folgenden Tabelle werden die Chromwerte des Nephelinsyenits und der Bauxite Typ I-IV zum Vergleich aufgeführt, wie sie bei Gordon und Murata angegeben sind. –Sämtliche hier

	(p.p.m. Cr)
Nephelinsyenit	1
Bauxit, Typ I	43
Bauxit, Typ II	89
Bauxit, Typ III	180
Bauxit, Typ IV	200

Einzelne Bauxite	(p.p.m. Cr)
(73) Bauxit, Gant, Ungarn, Harastoser Grube.	285
(74) Bauxit, Gant, Ungarn, Harastoser Grube (eisenarm).	400
(75) Bauxit, Epleny, Ungarn.	300
(76) Bauxit, Südfrankreich.	340
(77) Bauxit, Drnis, Dalmatien, Juguslawien.	805
(78) Bauxit, Istrien, Juguslawien.	445

untersuchten Bauxite zeigen hohe Chromgehalte. Dieses Ergebnis ist auch zu erwarten, wenn man den ohne weiteres plausiblen Fall annimmt, dass das Chrom wie das Aluminium bei der Bauxitbildung eine relative Anreicherung erfährt.

Eine besondere Beachtung verdienen die Proben (73) und (74). Sie stammen aus der gleichen Grube unterscheiden sich aber in ihrem Eisen- und Chromgehalt. Dabei ist der eisenreichere Bauxit chromärmer. Diese Feststellung ist deshalb interessant, weil sie dem übereinstimmt, was bei der Verwitterung des Granits von Kot beobachtet wurde. Denn dort wie hier stellt man fest, dass das Chrom nicht in den eisenreichen Partien des Gesteins angereichert wird. So kann

zusammenfassend gesagt werden: das Chrom reichert sich bei der Lateritbildung wie bei der Entstehung des Bauxits an. Ein gemeinsamer Gang von Eisen und Chrom kann dabei nicht beobachtet werden. –Die Tonmineralgruppen unterscheiden

Tonminerale	(p.p.m. Cr)
(79) Montmorillonit (Wyoming–Bentonit) Upton, westlich der Black Hills, No. 25, John C. Lane Tract (*Original material* siehe American Petroleum Institute (1951).	1
(80) Montmorillonit, Amory, Mississippi, No. 22 (*Original material*, API, 1951).	1
(81) Montmorillonit, Otay, Californien, H.24 (*Original material*, API, 1951).	1
(82) Montmorillonit, Santa Rita, New Mexico, No. 11 (*Original material*, API, 1951).	1
(83) Bentonitton, Krumbach, Bayern.	1
(84) Bentonitton, Tufarib, Orsawa, Rumänien.	1
(85) Montmorillonit + Feldspat, Verwitterungsprodukt des Hornblendeandesits, Panarea, Liparische Inseln.	5
(86) Nontronit, Garfield b. Spokane, H.33a (*Original material*, API, 1951).	6
(87) Nontronitton aus Klüften zwischen Basaltsäulen, Steinberg b. Meensen (Südniedersachsen).	12
(88) Illit, Morris, Illinois (*Original material*, API, 1951).	260
(89) Illit, Fithian, Illinois (*Original material*, API, 1951).	93
(90) Kaolinit, Murfreesboro, Arkansas (*Original material*, API, 1951).	14
(91) Kaolinit, Birch Pit, Macon, Georgia, No. 2 (*Original material*, API, 1951).	100
(92) Kaolin, Zettlitz, CSR.	10
(93) Kaolin, Schnaittenbach, Oberpfalz.	15
Der Kaolinit No. 7, Dixi Rubber Pit, Bath, South Carolina (*Original material*, API, 1951):	
(94) Gesamtgestein, alle Fraktionen.	74
(95) Fraktion: kleiner 2 μ.	72
(96) Fraktion: 2–60 μ.	74
(97) Fraktion: grösser 60 μ.	73

sich in ihrem Chromgehalt ganz beträchtlich. Am meisten Chrom enthalten die Illite, es folgen die Kaolinite und Nontronite, während die Montmorillonite nahezu kein Chrom enthalten.

Der Kaolin von Schnaittenbach ist nach Salger (1958) der das Gestein petrographisch untersucht hat, aus Biotit–Gneis und Arkose entstanden. Der Kaolin von Zettlitz wird von granitischem Gestein abgeleitet. Der Kaolinit von Macon, Georgia ist nach American Petroleum Institute (1951) ein Sediment, das durch Verwitterung eines feldspatreichen kristallinen Gesteins entstanden ist. Das Ursprungsgestein des Kaolinits von Murfreesboro ist noch nicht bekannt. Wheeler und Burkhardt stellen lediglich fest, dass es sich um ein Sediment handelt. Damit sind diese Kaolinite, soweit man über ihre Herkunft überhaupt etwas sagen kann, von sauren Eruptivgesteinen, oder von den entsprechenden metamorphen Gesteinen abzuleiten. Die Chromgehalte der Kaolinite, vor allem der Kaolinite von Macon,

Georgia und von Bath, South Carolina, liegen, wenn man sie vergleicht, höher als die Chromwerte der sauren Eruptivgesteine. Wenn es sich nicht gerade bei den hier untersuchten Proben um Kaolinite handelt, deren Ausgangsgestein ungewöhlich viel Chrom enthielt, darf man annehmen, dass bei der Bildung des Kaolinits eine Anreicherung des Chroms stattgefunden hat.

Um festzustellen, ob das Chrom, das man in den Kaoliniten findet, in allen Korngrössen gleichermassen vorkommt, oder ob es in den Erzen, die vornehmlich in der Korngrösse "grösser 60 μ" enthalten sind, angereichert ist, wurden die Fraktionen "kleiner 2 μ", "2–60 μ" und "grösser 60 μ" des Kaolinits von Bath neben dem Gesamtgestein untersucht. Die Analyse erbrachte das erstaunliche Ergebnis, dass alle Fraktionen praktisch gleich viel Chrom enthalten.

Die Illite, die man als Verwitterungsprodukte der Glimmer ansprechen darf, zeigen in ihrem Chromgehalt nichts Auffälliges. De Vore (1955a, b) gibt bei 39 untersuchten Biotiten 1–4700 p.p.m. Cr an und bei 10 Muskoviten 1–2800 p.p.m. Cr. Die Chromgehalte der Illite von Morris und Fithian liegen mit 260 und 93 p.p.m. innerhalb der Grenzen, die De Vore für die Glimmer angibt. Daraus darf man folgern, dass bei der Bildung der Illite der Chromgehalt gegenüber dem Ausgangsmaterial keine wesentliche Veränderung erfuhr.

In den Nontronitproben wird zwar nicht viel Chrom gefunden, doch ist ein Gehalt von 12 p.p.m. im Nontronit von Meensen so eindeutig festzustellen, dass man angehalten ist sich mit der Frage zu beschäfrigen, ob das Chrom—vielleicht an Stelle des Eisens—im Gitter des Nontronits sitzt, oder ob es aus den restlichen Bestandteilen der Probe stammt. Diese Frage lässt sich, wie ich glaube, gut beantworten, wenn man die Probennahme des Nontronittons vom Steinberg bei Meensen genauer betrachtet. Der Ton wurde aus den Klüften zwischen den Basaltsäulen herausgekratzt. Trotz vorsichtiger Arbeit können dabei bis zu 5% kleinster Basaltanteile in die Probe geraten sein.

Wenn man zu einer Überschlagsrechnung annimmt, dass die Nontronitprobe vom Steinberg bei Meensen 5% Basalt in kleinsten Teilchen enthält und ausserdem den Chromgehalt dieses Basalts, der bei 300 p.p.m. liegt, einsetzt, kommt man zu dem Ergebnis, dass die Probe lediglich auf Grund der basaltischen Verunreinigungen 15 p.p.m. Cr enthalten muss. Aus der Tatsache, dass die Probe nur 12 p.p.m. Cr enthält, kann man nur den Schluss ziehen, dass weniger basaltische Verunreinigungen darin sind als zur Berechnung angenommen wurden. Allgemein darf festgehalten werden, dass der Chromgehalt des Nontronits wohl nicht aus dem Gitter des Minerals stammt, sondern aus den Anteilen die die Probe sonst noch enthält.

Sieben Montmorillonite wurden untersucht und nur in einer Probe konnte etwas Chrom gefunden werden, während alle anderen Montmorillonite praktisch chromfrei sind. Dieses Ergebnis überrascht, denn es ist nicht einzusehen, warum der Montmorillonit im Gegensatz zum Kaolinit kein Chrom enthält.

Für den ausserordentlich niedrigen Chromgehalt des Montmorillonits gibt es grundsätzlich nur zwei Erklärungsmöglichkeiten. Entweder war schon das Ausgangsgestein chromfrei, oder das Chrom wurde bei der Bildung des Monmorillonits aufgelöst und weggeführt.

Um diese Frage zu beleuchten, ist es nötig, eine kurze Betrachtung über die

wahrscheinlichen Ausgangsgesteine der hier untersuchen Montmorillonite anzustellen. Die Angaben über die amerikanischen Montmorillonite stammen vom American Petroleum Institute (1951).

Der Montmorillonit von Upton, westl. der Black Hills ist aus einer nicht näher bestimmten vulkanischen Asche entstanden. Der von Amory, Mississippi ist eine Festlandsablagerung einer ebenfalls vulkanischen Asche. Der Montmorillonit von Santa Rita, New Mexico bildete sich rhyolithischem und andesitischem Tuff. Der von Otay, Kalifornien entstammt einer Lagerstätte, in der Asche und basische Ergussgesteine miteinander wechsellagern. Das Ausgangsgestein der Probe (85) ist ein Hornblende—Andesit, bei dem ein Chromgehalt von rund 50 p.p.m. zu erwarten ist. Der Montmorillonit tritt da als eine 2 m starke äussere Rinde auf.

Nach diesen Bemerkungen ist die Vermutung, das Ausgangsgestein sei schon chromfrei gewesen, nicht wahrscheinlich. Das Chrom muss demnach bei der Bildung des Montmorillonits aufgelöst und weggeführt worden sein.

Der Chromgehalt aller Pelite ist ausserordentlich ähnlich. 24 von 40 untersuchten Proben liegen zwischen 70 und 110 p.p.m. Cr (Abb. 2). Auch die anderen Proben liegen mit Ausnahme des Kupferschiefers von Albungen nahe um diese Werte herum. Die Tiefseetone wurden von Wedepohl (1960) in anderem Zusammenhang untersucht. Er bestimmte dabei auch ihren Eisengehalt. In Abb. 3 ist dieser neben dem Chromgehalt der Proben aufgetragen worden. Man stellt dabei zwar keinen gleichen, doch einen ähnlichen Gang dieser beiden Elemente fest. Dieser gemeinsame Gang kommt dadurch zustande, dass das Material gut durchmischt ist und die Tone am Meeresboden weithin einen ähnlichen Chromgehalt aufweisen. Mit dem Eisen verhält es sich ebenso. Wird nun der Tongehalt der Probe durch $CaCO_3$ verdünnt, nimmt das Eisen im gleichen Verhältnis ab wie das Chrom und es erscheint ein gemeinsamer Gang dieser beiden Elemente.

Vom Salzton von Reyershausen wurden die drei hier angeführten Proben aus der Korngrösse "kleiner 2 μ" von Niemann (1960) auf ihren Mineralgehalt und im Rahmen dieser Arbeit auf ihren Chromgehalt untersucht. Die Probe (115) enthält rund 50% Illit, 30% Chlorit, 15% Quarz und etwas Feldspat. Probe (116): 60% Illit, 30% Chlorit, 10% Quarz und wenig Feldspat. Probe (117): 60% Illit, 25% Chlorit und 15% Quarz. Der Vergleich des Mineralgehalts mit dem Chromgehalt ergibt, dass die Chromwerte mit zunehmendem Anteil an Tonmineralen steigen wie es die folgende Tabelle verdeutlichen mag. Daraus wie aus den Untersuchungen an zwei Verwitterungsprofilen über Sedimenten, die noch beschrieben werden, kann man folgern, dass das Chrom der Pelite in erster Linie in den Tonmineralen und zwar im Illit und Chlorit steckt. Der nächstwichtige Chromträger sind die Glimmer (Proben 191–194). Ein ganz geringer Teil Chrom könnte auch noch in den Relikten von Magnetiten und Pyroxenen enthalten sein. Da diese Relikte aber selbst nicht allzuviel Chrom enthalten und in den Peliten nur verstreut vorkommen, sind sie hier für das Chrom geochemisch uninteressant. –Die Chromgehalte der sandigen Gesteine variieren sehr viel stärker als das bei den Tonen der Fall war. Das ist auch leicht zu verstehen. Während bei den Tonen das Chrom in der Grundsubstanz des Gesteins lag, also in den Tonmineralen, enthält der Quarzanteil der Sande kein Chrom oder doch nur verschwindend wenig. Das

Pelite	(p.p.m. Cr)
Tiefseetone Nr. (98)–(114).	
(98) Lamont A 160 Nr. 8, 265 cm Sedimenttiefe.	70
(99) Lamont A 160 Nr. 8, 500 cm Sedimenttiefe.	97
(100) Lamont A 160 Nr. 8, 850 cm Sedimenttiefe.	80
(101) Lamont A 160 Nr. 7, 50 cm Sedimenttiefe.	88
(102) Lamont A 160 Nr. 7, 200 cm Sedimenttiefe.	97
(103) Lamont A 160 Nr. 7, 300 cm Sedimenttiefe.	89
(104) Lamont A 160 Nr. 7, 500 cm Sedimenttiefe.	94
(105) Lamont A 160 Nr. 7, 600 cm Sedimenttiefe.	94
(106) Lamont A 160 Nr. 5, 200 cm Sedimenttiefe.	94
(107) Lamont A 172 Nr. 14, 300 cm Sedimenttiefe.	101
(108) Lamont A 172 Nr. 17, 320 cm Sedimenttiefe.	109
(109) Albatross, Kern 255, 45 cm Sedimenttiefe.	60
(110) Albatross, Kern 255, 25 cm Sedimenttiefe.	64
(111) Albatross, Kern 255, 127 cm Sedimenttiefe.	74
(112) Albatross, Kern 255, 840 cm Sedimenttiefe.	74
(113) Meteorstation 305, 10–20 cm Sedimenttiefe.	75
(114) Meteorstation 283, 10–20 cm Sedimenttiefe.	82
(115) Salzton, Reyershausen (Org. Mat. Niemann, 1960). Probe Nr. 2933, "kleiner 2 μ".	96
(116) Dasselbe Gestein, Probe Nr. 3348, "kleiner 2 μ".	117
(117) Dasselbe Gestein, Probe Nr. 2941, "kleiner 2 μ".	106
(118) Dasselbe Gestein, Probe Nr. 2941, Gesamtgestein.	
(119) Durchschnitt von 36 europäischen, paläozoischen. Tonschiefern (Zusammensetzung s. Noll, 1934).	133
(120) Grüner Ton, Keuper, Ziegelei Friedland an der Leine.	73
(121) Ton, Keuper, Zaisersweiher b. Maulbronn.	83
(122) Ton, Lias α, Parensen b. Göttingen.	126
(123) Roter Rötel, Dogger β, Bohrung Eibenstock II (Material B. v. Freyberg, 1951), Franken.	138
(124) Rötelplatte, Dogger β, Bohrung Eibenstock II (Material B. v. Freyberg, 1951) Franken.	69
(125) Brauner Rötel, Dogger β, Bohrung Friedrich IV (Material B. v. Freyberg, 1951) Franken.	121
(126) Grauer Ton, Dogger β, Bohrung Pottenstein II (Material B. v. Freyberg, 1951) Franken.	115
(127) Ton, Barreme, Hoheneggelsen b. Hildesheim, (Org. Mat. Lippmann, 1955) Probe I.	132
(128) Ton, Barreme, Hoheneggelsen b. Hildesheim, (Org. Mat. Lippmann, 1955) Probe II.	154
(129) Glaukonitton, Kriede, Ülsen/Bentheim, Niederschsen.	109
(130) Glaukonitton, Kreide, Salzgitter, Bohrung Jemmeritz I.	100
(131) Glashafenton, Grossalmerode, Hessen, tertiäre Süsswasserbildung.	142
(132) Ton, Miozän, Bransrode, Meissner.	131
(133) Löss, Diluvium, Hedemünden an der Werra, Fuss des Fuchsberges.	51
(134) Interglazialton, Northeim b. Göttingen Ziegelei Kerr.	103
(135) Kupferschiefer, Zechstein, Schnepfenbusch Richelsdorf.	100
(136) Kupferschiefer, Zechstein, Albungen an der Werra.	353
(137) Kupferschiefer, Mansfeld, Zentrallabor Eisleben.	140

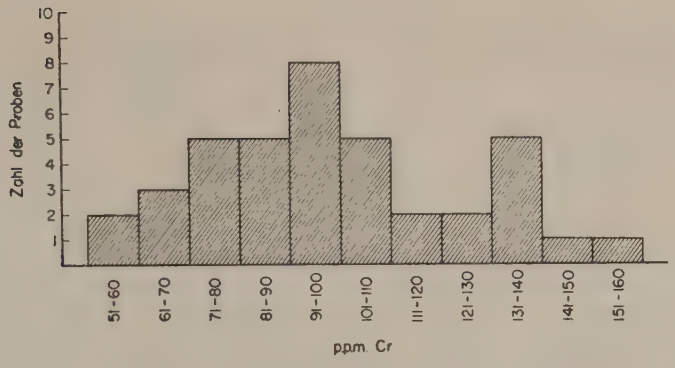

Abb. 2. Häufigkeit der Chromgehalte in den Peliten.

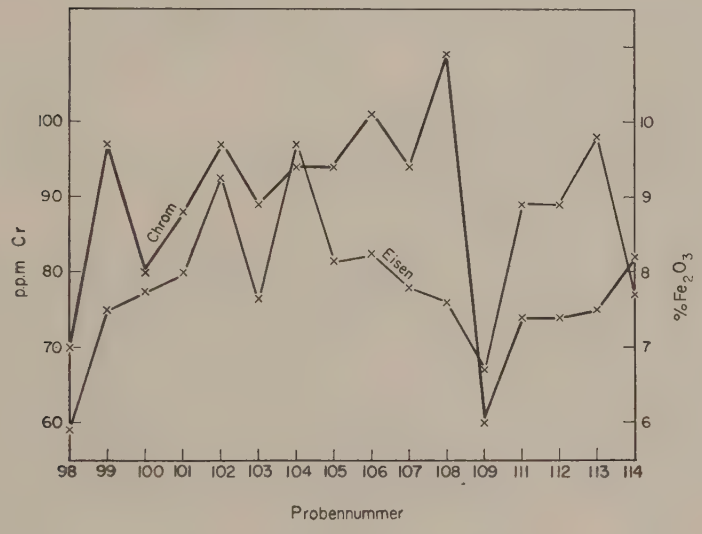

Abb. 3.

Probe	Cr (p.p.m.)	Fe_2O_3 (%)
(98)	70	5,91
(99)	97	7,51
(100)	80	7,77
(101)	88	7,97
(102)	97	9,28
(103)	89	7,63
(104)	94	9,72
(105)	94	8,16
(106)	101	8,25
(107)	94	7,80
(108)	109	7,63
(109)	60	6,71
(111)	74	8,90
(112)	74	8,90
(113)	75	9,80
(114)	82	7,70

Probe	Cr (p.p.m.)	Tonminerale (%)
(115)	96	80
(117)	106	85
(116)	117	90

Psamite und Psephite	(p.p.m. Cr)
(138) Durchschnitt von 11 deutschen Karbonsandsteinen (Zusammensetzung s. v. Engelhardt, 1936).	48
(139) Durchschnitt von 23 deutschen Buntsandsteinen (Zusammensetzung s. v. Engelhardt, 1936).	20
(140) Durchschnitt von 10 deutschen Quarziten (Zusammensetzung s. v. Engelhardt, 1936).	150
(141) Quarzit, Unteres Devon, Krebsberg b. Urbar.	123
(142) Taunusquarzit, Devon, Rochusberg b. Bingen.	65
(143) Ackerbruchbergquarzit, Goslar, Harz.	83
(144) Quarzit, miozän, Brunsberg b. Dransfeld nahe bei Göttingen.	1
(145) Unterer Buntsandstein, Freden an der Leine.	56
(146) Sandstein, Höllental südlich Hitzrrode.	12
(147) Sandstein, Unterrotliegendes, Bogental b. Nordhausen.	48
(148) Grüner Sandstein, Dogger β, Bohrung Pegnitz, Bergmannssiedlung (Mat. B. v. Freyberg, 1951) Franken.	45
(149) Kulm–Grauwacke, Okertalsperre (Org. Mat. Mattiat, 1960) Probe I.	22
(150) Kulm–Grauwacke, Okertalsperre (Org. Mat. Mattiat, 1960) Probe III.	40
(151) Kulmgrauwacke, Grosses Steimkertal, Harz (Org. Mat. Mattiat, 1960) Probe VI.	43
(152) Tanner Grauwacke, unt. Karbon, Andreasbachtal Harz.	93

Chrom der Sandsteine ist vielmehr in den Schwermineralen und den tonigen Anteilen zu suchen, die stark wechseln können.

Die Behauptung der Quarz im Sandstein enthielte kein Chrom, ist leicht zu beweisen, wenn man die Herkunft der Quarze betrachtet. Sie entstammen den sauren Eruptivgesteinen, und die Quarze dieser Gesteine, die selbst kaum Chrom enthalten, sind chromfrei.

Neben diesem indirekten Beweis kann man den Sachverhalt auch an den von Mattiat (1960) chemisch untersuchten Kulm-Grauwacken überprüfen. Dazu sind in der folgenden Tabelle die Silizium-, Aluminium-, Eisen- und Chromgehalte der drei Grauwacken miteinander verglichen. Die Tabelle zeigt, wie mit zunehmendem

Probe	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	Cr (p.p.m.)
(149)	77,2	9,6	2,6	22
(150)	65,2	16,6	5,1	40
(151)	63,1	16,7	5,8	43

SiO_2-Gehalt, also zunehmendem Quarzgehalt, der Chromgehalt abnimmt. Den gleichen Gang beobachtet man auch beim Eisen und beim Aluminium. Daraus muss man schliessen, dass das Chrom in den Eisen- und Aluminiummineralen der Grauwacke steckt und nicht in den Quarzen. –Die hier untersuchten

Kieselgesteine	(p.p.m. Cr)
(153) Feuerstein, Stevens Klint, Dänemark.	1
(154) Feuerstein, nördl. Wissower Kliniken b. Sassnitz, Rügen.	1
(155) Wachsopal, Kozelnik, Ungarn.	1
(156) Kulmkieselschiefer, Kieselschieferbruch, Wallau (Org. Mat. Hoss, 1957).	8
(157) Kieselsinter, Yellowstone Park.	1

Kieselgesteine sind alle nahezu chromfrei. Lediglich der Kulmkieselschiefer von Wallau enthält 8 p.p.m. Cr. Dieses Ergebnis ist auch ganz verständlich, denn nach Angaben von Hoss (1957) besteht dieser Kieselschiefer zu 10–15 % aus Illit. Zusammenfassend kann man feststellen, dass kein Chrom mit dem SiO_2 aus der Lösung ausgefällt wird. Die Karbonate sind ausgesprochen chromarm, und es ist

Karbonatgesteine	(p.p.m. Cr)
(158) Durchschnittsmischung von 32 deutschen Devonkalksteinen (Zusammensetzung s. v. Engelhardt, 1936).	12
(159) Durchschnittsmischung von 45 deutschen Jurakalksteinen (Zusammensetzung s. v. Engelhardt, 1936).	28
(160) Durchschnittsmischung von 16 deutschen Kreidekalksteinen (Zusammensetzung s. v. Engelhardt, 1936).	19
(161) Anthrakonit, Bornholm, Linse im Alaunschiefer.	2
(162) Dolomit, Hauptdolomit des Zechsteins, Scharzfeld, Harz.	2
(163) Dolomit, Hauptdolomit des Zechsteins, Roemerstein bei Bad Sachsa, Harz.	1
(164) Sandmergel, Muschelkalk, Göttingen.	46
(165) Steinmergel, Keuper, Ziegelei Friedland b. Göttingen.	10
(166) Serpulit, Thüste b. Hameln.	2
(167) Globigerinenschlamm, Lamont A 180 Nr. 74, 10 cm Sedimenttiefe.	
(168) Globigerinenschlamm, Lamont A 180 Nr. 74, 180 cm Sedimenttiefe.	20
(169) In HCl unlöslicher Rückstand des Kalks der Probe (160).	111

die Frage, ob dieses wenige Chrom im Gitter des Karbonats eingebaut ist, oder ob es im tonigen Anteil der Kalke steckt.

Um diese Frage zu klären, wurde die Durchschnittsmischung der 16 deutschen Kreidekalksteine näher untersucht. Es wurden 1,5 g des Gesteins drei Tage bei etwa 20°C mit 1 N HCl behandelt. Danach war das Karbonat gelöst, und es blieb ein Rückstand, der 0,24 g wog. Dieser Rückstand, der in erster Linie Tonminerale und etwas Quarz enthielt, wurde auf seinen Chromgehalt untersucht. Gefunden wurden dabei 111 p.p.m. Cr. Bezieht man diesen Wert auf das gesamte Gestein, dann ergibt sich ein Chromgehalt von 17,8 p.p.m. Das so erhaltene Ergebnis stimmt gut mit dem überein, was in Analyse (160) gefunden wurde. Damit ist

erwiesen, dass weder der Calxit noch der Dolomit—beim Dolomit zeigen es eindrucksvoll die Analysen (162) und (163)—Chrom in ihr Gitter aufnehmen. Das Chrom befindet sich in den nichtkarbonatischen Bestandteilen des Kalksteins, vor allem in den tonigen Anteilen.

Eisenerze	(p.p.m. Cr)
(170) Grüner Eisenoolith, Lias γ, Echte (Org. Mat. Harder, 1951).	1075
(171) Eisenoolith, Lias γ, Echte, zwischen 1 und 2 Sohle (Org. Mat. Harder, 1951).	775
(172) Chamositerz, Lias γ, Holtensen b. Göttingen.	585
(173) Chamositerz, Lias γ, Markoldendorf.	370
(174) Eisenoolith, Dogger β, Bohrung Unterklausen I (Mat. B. v. Freyberg, 1951) Franken.	90
(175) Toneisenstein, Dogger β, Bohrung Oberndorf I (Mat. B. v. Freyberg, 1951) Franken.	28
(176) Toneisenstein, Dogger β, Bohrung Unterklausen II (Mat. B. v. Freyberg, 1951) Franken.	71
(177) Eisenerz, Kreide, Salzgitter, Ilseder Hütte.	94
(178) Eisenerz, Kreide, Salzgitter, Ilseder Hütte (zwischen Geröll).	170
(179) Eisenerz, Kreide, Salzgitter, Grube Fortuna.	256
(180) Eisenoolith, Kreide, Salzgitter, Schacht Georg.	545

Der stark variierende Chromgehalt der Eisenerze beruht vornehmlich auf folgenden drei Gründen:

(1) Die Eisengehalte der Erze sind unterschiedlich und damit auch die Chromgehalte. Mit steigendem Kalkgehalt eines Erzes verdünnt sich dessen Chromgehalt.

(2) Die Gesteine der Abtragungsräume, aus denen das Eisen zugeführt wurde, boten unterschiedliche Mengen von Chrom an.

(3) Die Art, wie das Eisen in seine Lagerstätte transportiert wurde, war in den einzelnen Fällen verschieden. Im Zusammenhang mit diesem dritten Punkt muss auf den hohen Chromwert der Eisenoolithe von Echte hingewiesen werden. Nach Harder (1951) ist das Eisen in kolloidalem Zustand in diese Lagerstätte gebracht worden. Daraus darf man schliessen, dass das Chrom wie das Eisen kolloidal transportiert wird und so in Lagerstätten angereichert werden kann. Dabei zeigt sich kein wesentlicher Unterschied, ob es sich wie bei Probe (170) um chamositisches oder wie bei Probe (171) um hämatitisches Erz handelt. –Die Salze

Salze	(p.p.m. Cr)
(181) Zechstein, älteres Steinsalz, Reyershausen.	1
(182) Zechstein, Sylvin, Stassfurt.	1
(183) Zechstein, Polyhalit, Berlepschacht, Stassfurt.	1
(184) Zechstein, Gipsbreccie, Hundelshausen.	1
(185) Zechstein, dunkelgrauer Gips, Niedersachswerfen.	1

bieten in Bezug auf das Chrom ein sehr eintöniges Bild. Man kann nur feststellen, dass die durch Eindunsten des Meeres entstandenen Sedimente kein Chrom enthalten. Diese Tatsache ist insofern bemerkenswert als sie zeigt, dass das Chrom

nicht gelöst ins Meer gebracht wird, um in dort sich bildenden Mineralen auszufallen.

Zwei Verwitterungsprofile über Sedimenten

	(p.p.m. Cr)
(186) Zechsteinletten, Beberteich b. Barbis nahe Bad Lauterberg, Harz (Org. Mat. NORDMEYER, 1959) Originalprobe A 1.	56
(187) Dasselbe Gestein, Originalprobe A 2.	64
(188) Dasselbe Gestein, Originalprobe B 1.	72
(189) Dasselbe Gestein, Originalprobe B 2.	83
(190) Dasselbe Gestein, Originalprobe C.	74

Dieses Profil wurde von H. NORDMEYER (1959) eingehend untersucht. Es findet, ausgehend von den Zechsteinletten, die im Profil mit C angegeben sind, über die verschiedenen Stufen bis zu A 1, die der Erdoberfläche am nächsten ist, eine Verwitterung statt. Um festzustellen, in welchem Minerals sich das Chrom befindet und wie es wandert, ist es nötig, den Mineralgehalt der einzelnen Horizonte anzugeben. Aus dieser Tabelle lässt sich sehr schön erkennen, dass der Chromgehalt

Probe	Quarz (%)	Feldspat (%)	Glimmer (%)	Tonmin. (Illit) (%)	Chromgehalt (p.p.m.)
(186)	43	10	4	36	56
(187)	24	20	11	35	64
(188)	25	10	6	51	72
(189)	19	4	5	68	83
(190)	15	13	12	43	74

eines Horizontes abhängig ist von dessen Glimmer und Tonmineralanteil. Bei den Tonmineralen handelt es sich nach NORDMEYER vorwiegend um Illite. Der gemeinsame Gang von Chromgehalt und Schichtsilikaten (Glimmer + Illit) im Profil lässt sich nur erklären, wenn man das Chrom der Letten in diesen Mineralen eingebaut annimmt. In Abb. 4 ist die Summe von Tonmineralen und Glimmern als Funktion des Chromgehalts aufgetragen worden. Diese Darstellung lässt die Zusammenhänge sehr deutlich erkennen.

Das zweite Profil aus dem Buntsandstein vom Beberteich bei Barbis, das ebenfalls von NORDMEYER (1959) mineralogisch untersucht worden ist, zeigt ein ähnliches Ergebnis. Das Ausgangsmaterial ist der Sandstein C, der über die Stufen C 1, B, A 1 verwittert, wobei A 1 die oberflächennächste Schicht ist. Der Einfachheit halber wird hier der Chromgehalt gleich mit dem Mineralanteil der einzelnen Horizonte angegeben.

(191) bis (194) Bodenprofil auf unterem Buntsandstein, Bederteich b. Barbis nahe Bad Lauterberg, Harz (Org. Mat. NORDMEYER, 1959). Mit diesen beiden Profilen, die noch einmal sehr deutlich den Zusammenhang von Chrom und Glimmermineralen im Sediment demonstrieren, ist die Beschreibung einzelner Sedimentproben beendet. Ehe jedoch das Kapitel über die Sedimente völlig

Probe	Quarz (%)	Feldspat (%)	Glimmer (%)	Tonmin. (Illit) (%)	Chromgehalt (p.p.m.)
(191) C	31	17	7	13	28
(192) C 1	21	13	8	49	64
(193) B	17	10	10	50	65
(194) A 1	34	12	8	35	48

abgeschlossen wird, sollen noch einige allgemeine Bemerkungen über den Gang des Chroms bei der Sedimentbildung angeführt werden.

Das Chrom reichert sich bei der Bildung von Lateriten und Bauxiten und häufig auch in Eisenerzlagerstätten an. Dabei wird es aus dem Gestein gelöst und entweder gleich ausgefällt, oder, wie bei den Eisenerzlagerstätten, zusammen mit dem Eisen kolloidal transportiert.

Abgesehen von diesen drei Sonderfällen wird das Chrom nicht aufgelöst, sondern zusammen mit dem Mineral, in dem es sitzt, befördert. Die weitaus wichtigsten Transportminerale dieser Art sind Glimmer und Tonminerale (Illit und Chlorit). Das so transportierte Chrom wird nirgendwo besonders angereichert, es findet vielmehr den Weg in eine grosse Anzahl von Sedimenten.

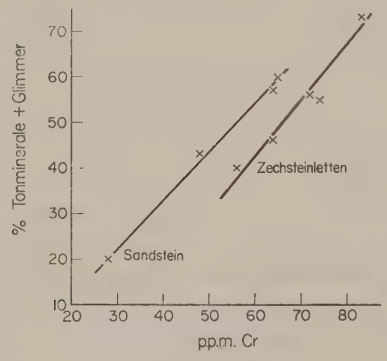

Abb. 4.

Metamorphe Gesteine

Zur Einleitung in das nun folgende Gebiet eignet sich die Untersuchung an einem Kontakt besonders gut, weil gerade sie Auskunft geben kann über die Mobilität des Chroms bei der Metamorphose. Deshalb sollen die Chromwerte des von Dreizler (1960) petrographisch untersuchten Kontaktes Kulmtonschiefer—Okergranit in der folgenden Tabelle angegeben werden. Die untersuchten Gesteine reichen von den völlig unveränderten Schiefern der Proben (195) und (196) bis zur Probe (200), die nur 1,50 m vom Kontakt entfernt ist und auch deutliche Kontakterscheinungen zeigt. Man stellt vom unveränderten zum veränderten Gestein einen leicht schwankenden, aber nicht systematisch veränderten Chromgehalt fest. Somit darf man behaupten, dass sich das Chrom bei diesem Kontakt als immobil erwiesen hat. Die Schwankungen im Chromgehalt zwischen 80 und 102 p.p.m. sind leicht erklärt, da die Proben aus verschiedenen Horizonten stammen.

	(p.p.m. Cr)
(195) Kulmtonschiefer, Grosses Bramketal, Harz (nicht metamorph) (Org. Mat. Dreizler, 1960) Probe (42).	99
(196) Kulmtonschiefer, Grosses Bramketal, Harz (nicht metamorph) (Org. Mat. Dreizler, 1960) Probe (42a).	100
(197) Kulmtonschiefer, Okerstrasse, 5,6 km unterhalb der Sperrmauer (Kontaktzone) (Org. Mat. Dreizler, 1960) Probe (45).	80
(198) Kulmtonschiefer, alte Okertalstrasse an der kleinen Brücke, Harz (Kontaktzone mit neugebildetem Cordierit) (Org. Mat. Dreizler, 1960) Probe (41).	87
(199) Kulmtonschiefer, unterhalb der Feigenbaumklippen, etwa 5 m vom Kontakt entfernt, Harz (Kontaktzone mit neugebildetem Cordierit) (Org. Mat. Dreizler, 1960) Probe (39).	82
(200) Kulmtonschiefer, Steinbruch an der Stiefmutterklippe, 1,50 m vom Kontakt entfernt, Harz (Kontaktzone mit neugebildetem Cordierit) (Org. Mat. Dreizler, 1960) Probe (33).	102

Kristalline Schiefer	(p.p.m. Cr)
(201) Orthogneis, Muggenbrunn, Schwarzwald.	3
(202) Paragneis, Muggenbrunn, Schwarzwald.	85
(203) Glimmerschiefer, Ehrenfriedersdorf.	6
(204) Labradorfels, Anclandsfjord, Norwegen.	1
(205) Bytownitfels, Italheimsklar b. Nöredal, Norwegen.	4
(206) Phyllit, Endschütz, Gera.	117
(207) Eklogit, im Gneis von Weissenstein, Fichtelgeb.	186
(208) Granat aus diesem Eklogit.	244
(208) Omphazit aus diesem Eklogit.	165
(209) Pyroxen–Olivinfels, Storegut, Melhedalsvand, Norwegen.	3410
(210) Olivinfels, Mysäter b. Kjölsdal, Nordrefjord Norwegen.	2240
(211) Olivinfels, Nordre Björkedal, Norwegen.	2250
(212) Olivinknolle aus Basalt, Hoher Hagen b. Göttingen.	1010
(213) Olivinknolle vom Dreiser Weiher, Eifel.	2470

Die Olivinknollen aus dem Basalt vom Hohen Hagen und vom Dreiser Weiher sind nur versuchsweise in der Rubrik der kristallinen Schiefer neben den Olivinfelsen aufgeführt worden. Es soll dabei nur auf den sehr ähnlichen Chromgehalt der Olivinknollen und der Olivinfelse hingewiesen werden.

Die Chromgehalte des Bytownit- und des Labradorfelses liegen unterhalb von 5 p.p.m. Dieser Chromgehalt entspricht in seiner Höhe dem, was in den Feldspäten der Eruptivgesteine gefunden wird. Der Pyllit von Endschütz zeigt mit seinen 117 p.p.m. Cr den Chromgehalt eines normalen Tones oder Tonschiefers. Ebenso zeigt sich das Chrom bei den Gneisen von Muggenbrunn im Schwarzwald als ein Element, bei dem sich keine Mobilität bei der Metamorphose nachweisen lässt. Der Orthogneis entspricht mit seinen 3 p.p.m. Cr einem Granit, während der Paragneis mit 85 p.p.m. Cr in der Grössenordnung der mergligen Tone liegt.

Im Zusammenhang mit den Gneisen von Muggenbrunn soll noch einmal ganz kurz die Frage beleuchtet werden, warum die Granite im allgemeinen kein Chrom enthalten, während einige Granitproben deutliche Mengen an Chrom aufweisen.

Bei der Betrachtung der Granite wurde vermutet, das in den Proben vorhandene Chrom könne von Verunreinigungen bei der Aufbereitung der Probe herrühren.

Bei der Betrachtung der Gneise von Muggenbrunn stösst man darauf, dass noch eine andere Erklärung für den hohen Chromgehalt einzelner Granite erwogen werden kann. Es ist nämlich nicht ausgeschlossen, und die Gneise von Muggenbrunn deuten darauf hin, dass es sich bei den chromhaltigen Graniten um ehemalige Sedimente handelt, die granitisiert wurden. Doch diese Frage kann nicht durch das eine Beispiel der Gneise von Muggenbrunn allein beantwortet werden. Dazu sind umfangreichere Untersuchungen nötig. In einer anschliessenden Arbeit wird diese Frage aufgegriffen und ausgiebig behandelt werden.

Amphibolite	(p.p.m. Cr)
(214) Amphibolit, Jekatrinburg, Ural.	492
(215) Quarzamphibolit, Niedere Tauern.	464
(216) Hornblende aus dem Quarzamphibolit, Niedere Tauern.	653
(217) Amphibolit, Miltitz, Meissen.	426
(218) Amphibolit, (angeblich geschieferter Basalt) Blatt Gusteham nahe Byholma.	304
(219) Amphibolit, Chichibu, Japan.	165
(220) Amphibolit, linkes Ufer der Salzach, zwischen Lend und Paxenbach.	138
(221) Amphibolit, Stein, Fichtelgebirge.	100
(222) Granatamphibolit, Geschiebe Westerland, Sylt.	97
(223) Amphibolit, Holenbrunn b. Wunsiedel, Fichtelfeb.	91
(224) Granatamphibolit, Valle de Po, Ober–Italien.	72
(225) Amphibolit, nahe Mesaba, Minnesota.	16
(226) Amphibolit, Felsbergkamm, Blatt Neuenkirchen, Odenwald.	3
(227) Glaukophanamphibolit, Valle de Varaita, Ober–Italien.	1

Die Tatsache, dass das Chrom bei der Metamorphose praktisch keine Mobilität aufweist, und die Feststellung, dass es in vielen Gesteinstypen in charakteristischer Menge vorhanden ist, eröffnet eine Möglichkeit, die Herkunft metamorpher Gesteine zu beleuchten.

Die Amphibolite streuen in ihren Chromwerten sehr stark. In der vorliegenden Tabelle sind Werte zwischen 1 und 500 p.p.m. zu finden. Bei den Amphiboliten, die über 150 p.p.m. Cr enthalten, dürfte es sich wohl um Orthogesteine handen, bei denen unter 20 p.p.m. wohl um sedimentäre Amphibolite, die aus Kalkmergeln hervorgegangen sind. Über die Amphibolite, deren Chromgehalt zwischen 20 und 150 p.p.m. liegt, kann man nichts Sicheres aussagen. Es kann sich bei ihnen vom Chromgehalt aus betrachtet um Ortho- als auch Paragesteine handeln. Zum Abschluss dieses Kapitels ist bie Frageangebracht: in welchen Mineralen der Amphibolite steckt das Chrom? Von den in dieser Ardeit untersuchten Amphiboliten konnte nur der Quarzamphibolit aus den Niederen Tauern in seine Minerale zerlegt werden. Er baut sich zu 70% aus Hornblende und zu 30% aus Quarz und Feldspat auf. Bei der chemischen Analyse wurden in der Hornblende 653 p.p.m. Cr gefunden, im Quarz und im Feldspat weniger als 1 p.p.m. Nach diesem Ergebnis befinden sich 457 p.p.m. von den 464 p.p.m. des Gesamtgesteins in der Hornblende. Das heisst, dass das gesamte Chrom der Amphibolite in der Hornblende steckt.

Der mittlere Chromgehalt der Lithosphäre

Zur Berechnung des mittleren Chromgehalts werden die Häufigkeitszahlen benutzt, die v. Engelhardt (1936) für die verschiedenen Gesteinstypen angibt. Für die Sedimente lassen sich nach den Analysen der vorliegenden Arbeit gute Mittelwerte angeben, da der Chromgehalt der einzelnen Typen nur in engen Grenzen schwankt. Sehr viel schwieriger liegt der Fall bei den Eruptivgesteinen.

Gestein	%–Anteil an d. Lithosphäre (%)	Cr–Gehalt der Gesteinsgruppe (p.p.m.)	Cr–Geh. d. Häufigkeit entsprechend (p.p.m.)
Tone, Tonschiefer	79,5	105	84
Sandsteine	12,0	58	7
Kalke	8,0	15	1
Dolomite	0,5	1	0
Durchschnitt der Sedimente:			92

Denn es ist nicht möglich, für die Granite einen wirklich brauchbaren Mittelwert anzugeben, weil viele Granite nicht mehr als 1 p.p.m. Cr enthalten, während andere Granitproben hohe, stark dovon verschiedene Werte aufweisen. Die Frage, die kaum beantwortet werden kann, ist: wie hoch ist der Prozentsatz der chromhaltigen Granite?

Die basaltischen Gesteinstypen zeigen stark wechselnde Chromgehalte. Der Mittelwert ist nicht mit genügender Genauigkeit zu bestimmen. Er wird zwischen 100 und 400 p.p.m. Cr liegen. Da sich beim Granit und beim Basalt solche Schwierigkeiten auftun, und ein ausreichend genauer Mittelwert nicht gefunden werden kann, soll die Berechnung des durchschnittlichen Chromgehalts der Eruptivgesteine unterbleiben.

Man darf annehmen, dass der Durchschnittswert der Eruptivgesteine dem der Sedimente sehr ähnlich ist. Daraus kann man folgern, dass der mittlere Chromgehalt der Erdkruste nahe bei 90 p.p.m. liegt.

Auerkennungen—Meinem verehrten Lehrer, Herrn Professor Dr. C. W. Correns darf ich andieser Stelle danken, dass er mich diese Arbeit durchführen liess und sie durch stetes Interesse mit zahlreichen Anregungen förderte. Fräulein Dr. P. Schneiderhöhn danke ich für vieles Analysenmaterial und wertvolle Ratschläge. Ebenso danke ich meinen Kommilitonen, die mir freundlicherweise Probenmaterial überliessen.

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Some aspects of the thermal evolution of the earth

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Abstract—Empirical data relating to the thermal history of the earth are examined. Recent astronomic and geochemical evidence strongly suggests that the earth formed by accretion from an initially low-temperature gas–dust cloud of solar composition. The distribution of U, Pb, Th and K within the earth imply that it passed through a melting or partial melting process about $4{\cdot}5 \times 10^9$ years ago. This conclusion is confirmed if the core is assumed to consist dominantly of iron–nickel. Formation of the core, which likewise occurred about $4{\cdot}5 \times 10^9$ years ago would liberate sufficient gravitational energy to cause melting. Evidence in favour of melting is also provided by analogy with meteorites.

An examination is made of possible causes of this early melting stage and it is concluded that gravitational energy is chiefly responsible. Radioactive heating does not appear to be important. A critical factor in the early heating and chemical evolution is the interaction of accreting dust falling with high velocity into the primitive reducing atmosphere surrounding the earth. Because of this interaction, a metallic phase is produced by reduction.

The distribution of temperature within the earth $4{\cdot}5 \times 10^9$ years ago will be given by the melting-point gradient. Recent data on the electrical conductivity of the mantle and the melting point of metals under high pressures suggest that the present temperature distribution is much less than the melting point gradient. This implies that the earth has cooled considerably.

The inferred cooling is consistent with present data on the abundance of radioactive elements in meteorites and in the earth, and also with possible modes of internal heat transfer—particularly convection and radiation.

Introduction

Problems connected with the thermal history of the earth have attracted the attention of numerous investigators during recent years, e.g. Slichter (1941), Urry (1949), Urey (1952), Jacobs and Allan (1954, 1956), Birch (1954), Lubimova (1958), Jeffreys (1958) and many others. However, the conclusions reached have in many cases been completely contradictory. The reasons lie, as usual in geophysics, in the basic assumptions made, and the resultant models which are set up for quantitative investigation. It therefore seems most desirable to assemble the available astronomical, geochemical and geophysical evidence relating to earth thermal history before setting up a model for mathematical treatment. This will be the object of the present paper.

The procedure in the following sections will be to discuss and evaluate the empirical data relating to temperature distribution within the earth at certain critical times since its formation. Conclusions from this discussion will be regarded as basic. Attention will then be directed towards the derivative problem—by what mechanisms of energy accumulation or transfer has the earth changed from one temperature distribution to the next? A criticism which can be levelled against some of the treatments referred to above is that they have tended to regard the second problem as the basic one. This has resulted in thermal histories which do not agree with fundamental geochemical and geophysical data.

I. Temperature Distributions at Selected Instants

1. *The initial state, prior to 4·55 aeons* ago*

There is a great deal of evidence which indicates that stars such as the sun have formed from initially cold clouds of dust and gas. Many astronomers—Weizsäcker (1944), Hoyle (1946), Ter Haar (1948), Edgeworth (1949), Kuiper (1956, 1957), Levin and Schmidt (1957), believe that the planets of the solar system have had an analogous origin. According to this view, the planets have formed from a gas–dust cloud of overall solar composition which had an initial temperature perhaps less than 50°K.

This view has received strong support from the work of Latimer (1950), Urey (1952), Chamberlain (1952) and Brown (1952). They have shown that certain elements and compounds which are found on the earth and in meteorites could not have condensed or been trapped if the earth (or meteorites) had formed from a hot gas of solar composition. On the contrary, the occurrence of this group is only explicable if much of the earth formed at a temperature around 0°C or below. The principal components involved are water, chlorine, nitrogen, carbon, sulphur and oxidized iron. These are gaseous, or reduced, in the presence of solar ratios of hydrogen to oxygen, at temperatures much above 0°C, and hence could not be trapped in an earth condensing from hot solar material.

On the basis of the above data, it is assumed in the present discussion that the earth has formed from an originally cold dust and gas cloud of overall solar chemical composition.

2. *Melting and differentiation of the earth*

The next stage is one during which the parental cold gas–dust cloud became unstable, allowing the non-volatile dust to collect together into planets. Various mechanisms concerned in this process, have been discussed by the authors previously cited. The causes of the initial instability and accretion are not well understood. Further discussion of the accretion process is given in Part II.

There is some strong and well-known evidence suggesting that during, or soon after accretion of the earth, a heating process occurred. This caused the entire earth to pass through a partially or completely molten stage, during a relatively short interval, about 4·5 aeons ago. The relevant evidence is as follows.

(a) Uranium and thorium are known to be strongly concentrated in the outer regions of the earth. This conclusion follows from the observed abundances of U and Th in crustal rocks, the surface heat-flow data, and the fact that the earth's mantle is not liquid. Birch (1958) has shown that if the earth contains the meteoritic abundance of uranium, then 70–90 per cent of the total uranium is at present in the crust. This distribution requires a thorough differentiation process affecting the whole of the mantle. (MacDonald, 1959).

Patterson (1956) and Masuda (1958) have shown that the "age of the earth" is 4·55 aeons. This age refers to the time when the upper mantle and crust could be regarded as a closed system, with a characteristic mean lead–uranium ratio. However, it has been pointed out that uranium has been very strongly enriched in

* Following the suggestion of Urey (1957) the term "aeon" meaning 10^9 years, has been adopted.

the upper mantle by a differentiation process. Since lead has very different crystal chemical properties to uranium, it would not be expected that a differentiation process which strongly enriched uranium near the surface of the earth would similarly enrich lead in precisely the same ratio. This conclusion is supported by isotope studies of common leads carried out by Russell (1956), Marshall (1957) and Masuda (1958) which show that U/Pb ratios within the upper mantle vary significantly, and that during differentiation processes, these elements tend to become separated. Thus it follows that the age 4·55 aeons refers to the time when differentiation of the whole mantle occurred, to give the present average U/Pb ratio observed in the upper mantle–crust system.

Such a differentiation of U and Th is most readily explained if the whole earth passed through a molten or partially-molten stage during a relatively short time interval, 4·55 aeons ago. In this manner, U, Th and other elements such as potassium could be concentrated by fractional crystallization. The writer has not yet seen a satisfactory alternative mechanism proposed, which does not involve melting.

(b) The earth most probably possesses an iron–nickel core.* This must have differentiated from the initially-uniform accreted planet. This differentiation affects the lead/uranium ratio of the residual silicates, since the metal carries down significant quantities of lead, but no uranium. Therefore the segregation of the core must have occurred at or before 4·55 aeons ago. Such a segregation is most easily understood if the earth was molten. Urey (1952), however, has suggested that segregation of the core could occur if the metal was molten, but the silicates were solid. Under such conditions it might be possible for molten iron to collect in bodies large enough to sink through the solid silicates. On this model, the minimum average temperature of the mantle required for the segregation would be around 2000°C. However, Urey (1952) has shown that such a segregation would liberate 800 cal/g of gravitational energy for the whole earth. Making a correction for strain in the interior, Birch (personal communication) suggests a smaller value, of 600 cal/g. This additional heat evolution would cause melting throughout the earth. Thus we may conclude that the occurrence of an iron core necessitates that the earth passed through a molten stage, 4·55 aeons ago. It is natural to associate this with the differentiation of U, Th and K as part of the same overall process.

(c) The chemical evolution of the meteoritic planet (Ringwood, 1959, 1960) has been similar to that of the earth in many ways. It passed through a stage 4·55 aeons ago when lead was separated from uranium by the differentiation of a metallic phase. The textures of meteorites show clearly that this separation was accompanied by a melting process. Analogy with the earth is immediately suggested.

It would appear that the points (a), (b) and (c) above are most easily explained

* Ramsay (1948) has suggested that the core is a metallic form of olivine. This suggestion is no longer attractive for many reasons. Elsasser (1950), Birch (1952), Macdonald and Knopoff (1958). Perhaps the chief argument against it is the requirement that the non metal–metal transition at the core boundary involves nearly a 100 per cent increase in density. There is no justification for this assumption. The Ramsay hypothesis is, in addition, inconsistent with the meteoritic relative abundances of iron to silicon and magnesium. If a meteoritic model is assumed, then the Ramsay hypothesis is automatically excluded. It may be remarked that Lubimova (1958) takes meteoritic abundances of U, Th and K in her model, but then goes on to accept the Ramsay model.

if the earth had melted and differentiated 4·55 aeons ago. No plausible explanation of these points has yet been made on the basis of an unmelted earth. Until one is forthcoming, a melting process must be accepted as most probable.

Some recent discussions of earth thermal history have attempted to show that the earth has never passed through a molten stage, and is still heating up. This conclusion depends critically upon *ad hoc* assumptions connected with the particular model used—particularly the depth variation of thermal conductivity

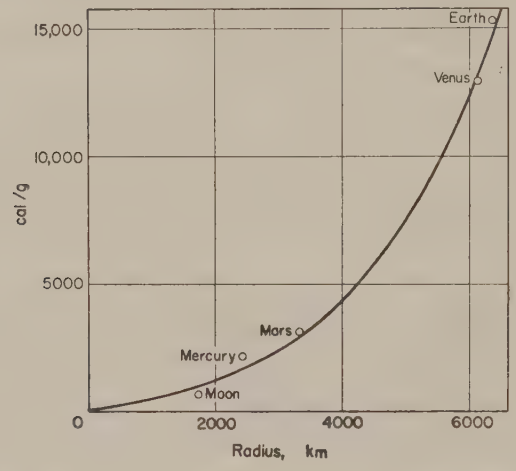

Fig. 1. Melting point curve (I) and probable present temperature distribution (II) in the mantle.

and radioactivity. When conclusions based upon such assumptions contradict empirical evidence on thermal history, they must be regarded with considerable reserve.

In the following discussion, we accept the empirical evidence relating to a melting stage. It therefore appears most likely that the initial temperature gradient in the earth will be the melting gradient.

Boyd (1958) has reported some preliminary results on the effect of a considerable pressure range on the melting point of diopside. Since diopside is closely related to the minerals which probably occur in the mantle, this data is most significant. In Fig. 1, the Simon equation (Simon, 1937) has been applied to Boyd's results. This probably gives the best available extrapolation of the melting point of diopside at extreme pressures—and hence, of the melting point gradient in the mantle. An independent estimate of this gradient by Uffen (1952) based upon seismic data and solid-state theory agrees well with the Boyd–Simon curve. It seems possible that these are minimum estimates since phase changes between 300 and 900 km will increase the melting gradient.* Against this it may

* Bowen and Schairer (1935) give dT/dP for olivine as 0·0045°C/bar. This estimate is based upon a Δv value derived by extrapolation of refractive indices in the system MgO–FeO–SiO_2. The extrapolation was linear and plotted against weight per cent. This is incorrect since the refractive index should have been plotted against mole per cent. When corrected in this manner, dT/dP is found to be 0·007°C/bar. Olivine probably inverts to a spinel structure at a relatively shallow depth in the mantle (Ringwood, 1958) with 11 per cent increase in density. Taking Δs for the olivine–spinel transition from the data of Dachille and Roy (1959) for the same transition in Mg_2GeO_4, we find dT/dP for the high-pressure phase is 0·014°C/bar. Evidently a considerable increase in melting-point gradient is caused by the phase change.

be argued that the mantle is a complex system, and appreciable lowering of melting temperatures will be caused by solid solution and eutectic effects. This lowering is most unlikely to exceed 500°C however, and will probably be more than compensated by the phase transition effect.

In Fig. 1, the melting point gradient is seen to run from 1400°C at the surface, to about 6000°C at the core–mantle boundary. We may regard this as the temperature distribution within the earth at stage (2) of the thermal history.

3. *The present state*

In this section the temperature distribution within the earth at present will be discussed. In Fig. 1 a curve illustrating this distribution has been hazarded. Needless to say it is highly tentative. Despite the uncertainties involved, useful conclusions can be drawn. The curve is based upon the following data.

(a) Temperature at the base of the continental crust (Mohorovicic Discontinuity) is estimated between 400°C and 600°C by Birch (1955). This is based upon observed surface heat flow, crustal structure and plausible amounts and distributions of radioactivity. Allowance for the decrease of thermal conductivity with increasing temperature suggests that the upper limit of 600°C might be more common.

(b) It is widely believed that basaltic magmas are generated in the outer mantle by fractional melting. Likely depths are 50 km to 200 km. Verhoogen (1954) has shown that a temperature of 1400°C would be required. Since basalt has been erupted very abundantly throughout geologic time and space, it would seem that much of this zone of the earth has temperatures approaching, but somewhat less than 1400°C.

(c) The electrical conductivity of the outer mantle is fairly well known (Lahiri and Price, 1939). Tozer (1959, and personal communication) has shown that the observed value places an *upper* limit of 1700°C for the average temperature at 400 km. This value appears to be well founded.

(d) From the electrical conductivity distribution in the lower mantle, Tozer (1959) estimates that the region between 1000 km and 2900 km has a temperature above 3000°C. However, this calculation depends upon a somewhat uncertain estimate of the conductivity constants for the close packed spinel-type silicates in the lower mantle, and it is possible that the temperatures may be appreciably lower than estimated.

(e) The inner core is probably solid (Bullen, 1958) and is most plausibly interpreted as nickel–iron solidified under pressure (Birch, 1940, 1952). This allows an estimate for the temperature to be made from the pressure effect on the melting point of iron. Recently Strong (1959) has determined this effect over a range of 96,000 atm. Extrapolation of his results with the aid of the Simon (1937) equation leads to melting temperatures of 2630 $\pm$ 200°C at the inner core boundary and 2340 $\pm$ 200°C at the core–mantle boundary. The real temperature at this latter boundary would therefore lie somewhere between these limits. These values are surprisingly low and somewhat in conflict with (d). MacDonald and Knopoff (1958) and Ringwood (1959) have suggested that the core contains substantial quantities of silicon—approximately the composition $(Fe\ Ni)_2\ Si$. It seems quite

possible that this compound would possess a higher melting gradient than iron, which is lower than that of all other metals measured (Strong and Bundy, 1959). In this case a temperature around 3000°C at the core—mantle boundary would not be unreasonable.

Using the data discussed in preceding paragraphs, a depth–temperature curve for the present earth has been constructed (Fig. 1). It is observed to be very much lower than the melting curve. Although both curves have a considerable range of uncertainty it seems probable that their relative positions are approximately correct. This conclusion is based primarily upon the experimental data which show that the melting points of silicates increase much more rapidly with pressure than those of incompressible metals—particularly iron, together with the assumption that the inner core consists of solidified nickel–iron. Further evidence indicating that the present temperature distribution within the earth is below the melting curve will be mentioned in Section 6.

Since the melting curves give the temperature distribution in the earth 4·55 aeons ago, it follows that a considerable amount of cooling has occurred in the earth in order to reach its present state. The thermal history of the earth, as inferred from empirical geochemical and geophysical data in the previous sections may thus be summarized.

A parental cold dust cloud became unstable and accreted into a large central body—the earth, which warmed up, melted and differentiated 4·55 *aeons ago, subsequently cooling considerably to its present state.*

This sequence of events now raises two problems:

(i) What factors controlled the heating of the earth from an initially cold state, so that it melted and differentiated?

(ii) What factors controlled the cooling of the earth from the original melting gradient to its present state?

II. Heating and Cooling Mechanisms

Before discussing a detailed heating mechanism, attention should be drawn to an important correlation. The age of the meteorite planet, given by lead–lead, strontium–rubidium and potassium–argon methods is the same as that of the differentiation and final consolidation of the earth—namely 4·55 aeons. This implies that melting, differentiation, and crystallization processes were essentially simultaneous in both bodies. However, the meteorite body was certainly much smaller than the earth (Urey, 1956; Lovering, 1957). Accordingly the increase in melting point due to pressure in the earth was much larger than that in the meteorite body. It follows that a larger amount of heat per gramme is required for melting the earth. Investigation of this effect using the melting curve (Fig. 1) shows that the earth required about twice as much heat per gramme as the meteorite body.

This observation suggests that the earth possessed larger heat sources than the meteoritic body. It is clear that radiogenic heat supplied by K, U and Th could not have been important unless the close correspondence in age ($\pm 7 \times 10^7$ years, Patterson, 1956) between meteorites and earth is purely coincidental. This series would take much longer to melt the earth than to melt the meteoritic body from an initially-cold state. A further large amount of heat must have been required in the

earth to account for its high degree of chemical reduction, compared to chondrites (Ringwood, 1959; MacDonald, 1959).

The writer (Ringwood, 1959) has recently discussed the chemical evolution of planets. Included was a brief discussion of possible heat sources responsible for melting and reduction. These may be classified into two groups—"internal sources" which operate after the dust cloud has accreted into a planet and "external sources" which operate before and during the accretion process. In the previous discussion it was suggested that the important heat sources were of internal origin. These included:

(i) radiogenic heat due to the K–U–Th series;
(ii) radiogenic heat due to nuclides with short half-lives;
(iii) chemical heating;
(iv) heat evolved during the formation of metallic cores.

The external source considered was the gravitational potential energy of the dispersed dust. It was suggested that the principal importance of this source was in regulating the accretion temperature and thus controlling the amount of "chemical heat" which could be incorporated.

The writer now believes that it is impossible to satisfy the demands of all planets with the same formula, and that substantial modifications of previous models are required. It is now suggested:

(a) that heating in small planets—Mars, the moon and meteoritic, is due to "internal sources" above;
(b) that heating in the earth and Venus is due principally to external and internal heating of gravitational origin;
(c) that Mercury is a special case, owing to its proximity to the sun.

4. *The heating process*

(a) *General.* We start with a cold cloud of dust and gas, either captured by the sun (Weizsäcker, 1944; Ter Haar, 1948; Edgeworth, 1949; Levin and Schmidt, 1957) or thrown off from the sun whilst it was undergoing its Kelvin contraction (Kuiper, 1957; Hoyle, 1955; Burbidge and Burbidge, 1958). The cloud develops as a disk surrounding the sun, contracting perpendicularly to its axis of rotation. Eventually gravitational instability and turbulence set in, and the disk breaks up to form a series of smaller clouds—parental to the planets. The details of this process are poorly understood.

We now consider the development of the earth from its parent gas–dust cloud. For some reason, as yet unknown, the cloud becomes unstable. Dust particles, when they collide, begin to stick to one another instead of flying apart or volatilizing, and thus a series of condensations or planetisimals are formed. Current estimates suggest that these condensations may have varying sizes up to perhaps 100 km diameter. However, they are continually colliding and being pulverized so there will be a wide range of size distributions within the dust cloud. Eventually a fluctuation arises such that a large condensation forms. This is sufficiently large to exert substantial gravitational attraction upon other condensations and not be broken up by the resulting collisions. When this stage is reached the primary accretion process commences.

(b) *Size distribution of condensations.* It is to be expected that there will be a complete spectrum of sizes from the smallest dust particles (10^{-14} g) to large condensations, say, 10^{20} g. There will be essentially a kinetic equilibrium owing to fragmentation of condensations by collisions, with accompanying growth and accretion. Whether this will give rise to any preferred size distribution is unknown. Perhaps a reasonable assumption is to assume a simple size distribution such as

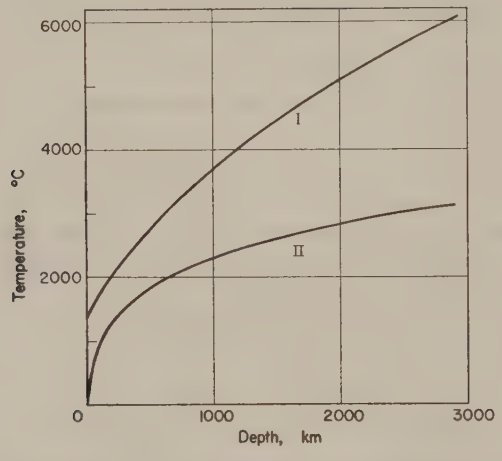

Fig. 2. Relationship between energy of accretion (cal/g) and radius during the growth of a terrestrial planet.

that approximately displayed by meteors (Lovell, 1954) over a size range of ten magnitudes, and perhaps of forty magnitudes. This covers particles ranging in mass from 10^{-14} g to 500 g. Within this range there is approximately an equal mass of meteors entering the earth's atmosphere for each magnitude. The corresponding assumption in the case of the dust cloud would be equal masses of condensations for any given series of logarithmic size intervals.

(c) *Chemical composition of dust.* The cloud is assumed to be cold ($\leqslant 0°C$) and composed of the solar abundance of elements. Under these conditions the non-volatile compounds will be completely oxidized (Section (1)).

The dust particles and condensations consist of non-volatile oxides and silicates, together with ice such as H_2O, NH_3 and CH_4. In addition, carbonaceous compounds possessing low volatility also collect with the dust. This is shown by the chemistry of meteorites (Ringwood, 1959, 1960) and is a most important feature.

(d) *Conditions during accretion.* According to the model, dust and condensations begin to fall on the surface of the central nucleus. These possess gravitational potential energy per gramme with respect to the nucleus given by GM/R where G is the gravitational constant, M is the mass of the nucleus and R is its radius. The accretion energy thus increases roughly as the square of the radius. There is accordingly a very large difference in accretion energy between the earth and Venus on the one hand and Mars, Mercury and the moon on the other (Fig. 2). It is seen that the final energies of accretion for the earth and Venus are very large

indeed, around 15,000 cal/g, and the possibility arises that this could be an important energy source, causing thermal and chemical effects.

When accreting matter falls on the surface of the planet, its energy is rapidly converted to heat. This may be dissipated as radiation, or it may be absorbed by endothermic chemical reactions. In Section (1), reasons were advanced for believing that the primitive dust and condensations consisted of oxidized meteoritic material, together with ices of H_2O, NH_3 and CH_4, and non-volatile carbonaceous material. Such an assemblage is stable at low temperature. However, when heated, significant chemical changes occur. The first effect is to evaporate the ices NH_3, CH_4 and H_2O. In the latter case this absorbs about 600 cal/g. At higher temperatures ($>500°C$), oxidized iron becomes reduced by the carbonaceous material.

$$2FeO + C = 2Fe + CO_2 \qquad \Delta H = 200 \text{ cal/g}$$

At temperatures of 1600°C and above, carbonaceous material reacts with SiO_2 and MgO, reducing them to metals. Heat absorbed is around 2000 cal/g.

The details of the process are likely to be incredibly complex—the heat balance being determined by the relative amounts of ices to non-volatile dust, the kinetics of the chemical reactions, and the partition of thermal energy between radiation and endothermic chemical reactions. Nevertheless the general outline seems clear. The central nucleus, with low gravitational energy, would remain cool and oxidized, and would probably contain substantial amounts of volatiles. Perhaps the size of this nucleus would be about that of Mars. As the size increases, and the gravitational energy increases, volatiles are driven off as the condensations fall upon the nucleus.

A critical stage of evolution is reached when the nucleus is large enough to retain some of the escaping volatiles in an atmosphere. The situation is then radically changed—instead of dust falling on a cold solid surface, it is falling into a blanket of gas, and the interactions are fundamentally different. Some idea of what is to be expected in the earlier stages, whilst the atmosphere is relatively small, is provided by the study of meteors and meteorites.

We now assume that condensations, covering a range in size from 10^{-14} g to, say, 10^{20} g, are falling upon the nucleus which has developed a substantial atmosphere. The subsequent behaviour is largely controlled by the particle sizes.

Condensations ranging from 10^{-14} to 10^{2} g probably behave similarly to meteors. When they hit the outer atmosphere of the earth, they are completely evaporated (Lovell, 1954) at very high temperatures. Ionization and radiation occur, followed by chemical recombination of the evaporated atoms. *However in the case of an accreting planet, with a high rate of infall of matter, the recombination takes place at high kinetic gas temperatures in a reducing atmosphere.* Accordingly the chemical equilibria are considerably altered. The oxidized dust and condensations are reduced to metal by the accompanying carbonaceous compounds, methane, etc. (Ringwood, 1959).

$$2FeO + C = 2Fe + CO_2$$

$$SiO_2 + 2C = Si + CO$$

$$4FeO + CH_4 = 4Fe + 2H_2O + CO_2, \quad \text{etc.}$$

The evaporated atoms thus recombine in the outer atmosphere to form a highly-reduced metal phase which slowly sinks towards the surface of the planet as fine dust and globules.

Larger condensations, from 10^2 to 10^{12} g behave more like meteorites. When they hit the atmosphere they suffer ablation at the surface, where a considerable amount of their mass may be removed in the form of fine droplets, produced by friction of the meteorite surface with the atmosphere. These droplets, since they are forming in the presence of carbon, and a reducing atmosphere containing methane, are also strongly reduced to metal. If the meteorite is in a certain size range, it may dissipate most of its kinetic energy by means of the ablation process at its surface, and slow down to terminal velocity. Whilst the atmosphere is still small, such bodies may reach the earth's solid surface with their interior relatively cool. However, in the later stages, with a larger atmosphere, these bodies would be completely ablated before they reached the surface. Since the condensations are likely to be fragile, they will probably break into small pieces which ablate readily.

An indication of the probable behaviour of the largest accreting condensations ($\geqslant 10^{12}$ g) is given by the behaviour of large meteorites. These travel through the atmosphere without appreciable losses of velocity. Their energy is liberated as an explosion when they collide with the surface (Baldwin, 1959; Nininger, 1956). Under these conditions a considerable amount of the meteorite is vapourized at very high temperatures. Accordingly in the presence of reducing agents, chemical reduction as discussed above will occur.,

The mass of CO_2, H_2O and CO produced during the reduction process may amount in the case of the earth to 20 per cent of the mass of the non-volatile metals and silicates which finally collect. Thus the atmosphere which is developed by the above processes will be of enormous size compared to the atmosphere at present on the earth. At the solid surface the pressure may be of the order of 300,000 atm at a density of 2 g/cm^3. The processes discussed above refer to the interaction of accreting condensations with a small atmosphere. The same mechanisms will occur in the upper region of the large atmosphere. However, it is probable in the latter case, that no solid, unreduced, material would reach the surface of the earth, since all the reduction and heating mechanisms previously discussed will be greatly magnified and intensified.

Summarizing, when accretion occurs of material with the suggested chemical composition, the early stage will give rise to a relatively cool, oxidized nucleus, containing volatiles. As the size of the planet grows, the energy of accretion increases, so that volatiles are driven off as the dust condensations collect on the surface. Next the size of the planet becomes sufficiently large to retain these volatiles in an atmosphere. After this stage, no matter what the particle size of the condensations, a very large amount of the material which accretes will have been subjected to high temperature. In the presence of accompanying reducing agents, chiefly carbon and methane, this material will be reduced to metallic alloys, principally of iron, nickel and silicon. It is suggested that this stage was reached upon the earth and Venus, but perhaps not upon the other terrestrial planets.

Consider the situation following such an accretion process. The outer regions

of the earth will be metal-rich and dense*, compared to the interior, composed of oxidized silicates and volatiles. Such a state is gravitationally unstable. Convective overturn must follow, leading to a sinking of the metal-rich outer region into the centre. This causes further evolution of heat due to the energy of gravitational rearrangement. In Section (1) it was pointed out that the formation of a core from an initially homogeneous earth would evolve 600–800 cal/g for the whole earth. Since the initial state is already unstable in the present case (being denser at the top than the bottom) the amount of evolved gravitational energy will perhaps be double the above estimate. This would be sufficient to melt the earth. Since the overturn is likely to be accelerated as internal temperature rises, the whole process is likely to be catastrophic.

A further heat source is available. Convection and melting cause mixing of the highly-reduced metal phase with the oxidized interior. These regions are out of chemical equilibrium and react endothermically when they come in contact.

$$\underset{\text{metal}}{\text{Si}} + \underset{\substack{\text{(oxidized}\\\text{interior)}}}{2\text{FeO}} = \text{SiO}_2 + 2\text{Fe}(-\Delta H = 500 \text{ cal/g})$$

It is probable that this reaction will not proceed to completion because of kinetic factors, leading towards a substantial concentration of metallic silicon in the earth's core. Consequent disequilibrium at the core–mantle boundary may give rise to electrolytic effects and localized electric currents (Ringwood, 1959).

An attempt has been made to make the above discussion as general as possible. It was concluded that melting of the earth would occur throughout a variety of accretion conditions. There is an additional factor leading towards the same conclusion. This concerns the rate of accretion.

The surface temperature on the accreting planet is determined by the balance between the rate of accretion and the rate at which energy can be radiated away. The first factor has been considered by Hoyle (1946) and Ter Haar and Wergeland (1948), who point out that the rate of accretion will increase rapidly with the mass of the nucleus. Ter Haar suggests that

$$\frac{dM}{dt} = KM^2, \quad \text{where } K = 2 \times 10^{-41} \text{ g}^{-1} \text{ sec}$$

whereas Hoyle suggests that the time required for a given mass to double itself by accretion is 10^5 years.

On these assumptions the temperature of a body the size of the earth could exceed the melting point during the latter stages of accretion, in which case the net result would be similar to that discussed in the previous section. However, this result depends critically upon the time constants assumed. Safronov (1954) does not believe that the time constant will be as short as that suggested by Ter Haar and Hoyle and therefore maintains that the earth would not have melted according to this simple model.

There is one factor not taken into account by these authors, which restricts the rate at which energy is radiated away from the earth, and thus increases the surface temperature. This factor may well have been of considerable importance.

* Referred to zero pressure.

The accretion process with accompanying reduction creates an enormous atmosphere of H_2O, CO_2 and CO as mentioned in the previous section. Much of the energy of accretion is liberated deep within this atmosphere which can function as an effective insulator—since both H_2O and CO_2 absorb strongly in the infra-red. Clearly such an effect* could magnify very substantially the possibility of direct melting of the earth (and Venus) during accretion.

(e) *Escape of atmosphere.* The hypothesis previously presented implies the production of an enormous atmosphere of CO_2, CO and H_2O due to reduction process on the primitive earth. This may amount to one-fifth of its mass. A critical requirement of the hypothesis therefore, is that this atmosphere was somehow dissipated at an early stage. Mechanisms which may have been concerned are suggested below. It is possible that more than one may have operated simultaneously.

Before proceeding, it is worth remarking that the present atmosphere is much smaller than would be expected if the earth had formed by accretion. Because of the high accretion energies involved, this process necessarily implies that most of the earth has been subjected to very high transient temperatures, which would have caused complete outgassing. This would suggest that some escape mechanism has in fact existed. Consistent with this are the findings of Suess (1949) and Brown (1952) that the earth has been severely depleted of its original inert gases. Factors which may have been responsible for escape are:

(i) intense solar radiation (Kuiper, 1956);
(ii) a high rate of rotation in the past (Suess, 1949);
(iii) magnetohydrodynamic surface interactions (Burbidge and Burbidge, 1955).

It seems possible that all three of these mechanisms may have been involved.

Kuiper (1956) has suggested that dissipation and escape of gases from the protoplanet was caused by primitive solar radiation. Escape of H_2O, CO_2 and CO from the earth may possibly be due to the same cause. Prof. W. Baade has pointed out to the writer that the Kelvin-stage contraction of stars like the sun might not be a smooth, uniform process. It is believed that T-Tauri stars represent the later stages of this contraction, before the main sequence is reacted, and nuclear fuel burning commences. (Herbig, 1957a, b; Armbartsumian, 1957). These stars are characterized by strong flares and outward ejection of matter. The cause is obscure. Burbidge and Burbidge (1955) suggest magnetohydrodynamic surface processes. These flares are of enormous magnitude and intensity compared to normal solar flares. If the sun had passed through such a stage, which seems entirely plausible, loss of planet atmospheres could well have been caused by intense solar particle radiation due to these flares. At any rate it seems likely that there are many new and unknown phenomena involved here, which may be of geophysical importance, and further advances should be possible as astronomers learn more about the details of the Kelvin contraction. The earth may possibly have dissipated its atmosphere by a similar mechanism to that displayed by T-Tauri stars.

* This point was first suggested to the author by Professor G. J. F. MacDonald of UCLA. It has also been recently made by Jeffreys (1958), p. 285.

Suess (1949) and Kuiper (1957) have pointed out that a high rate of rotation of the earth will greatly facilitate the escape of gases. Present ideas on the origin of the earth–moon system suggest that the primitive earth may have rotated much more rapidly than at present, and hence this factor may have played an important role.

The possibility that loss of the primitive atmosphere was causally related to early rapid rotation of the earth has some interesting but highly-speculative aspects which may be worth exploring. If the earth formed in a turbulent dust cloud, one might expect a higher rate of rotation than it now possesses. The same applies to the other terrestrial planets, particularly Venus.

The surface temperature of the earth after formation is likely to be very high. We recall that initially, before convective overturn, the outer regions will be metal-rich and therefore electrically conducting. Owing to the high temperature the non-metallic region will also probably form a good ionic and electronic conductor. At the same time, the primitive hot and dense atmosphere of H_2O, CO_2, CO and other solutes will function as a conductor, owing to thermal and electrolytic ionization. The atmosphere will attempt to convect, and it is conceivable that a dynamo action may ensue, leading to electromagnetic coupling between earth and atmosphere. Both would therefore rotate with the same angular velocity.

Now consider the situation when convective overturn occurs in the earth leading to segregation of metal phase and formation of a core. Segregation of the core, as suggested in Section (5), will probably be catastrophic since the energy released greatly decreases the viscosity and correspondingly increases the segregation rate. This rearrangement results in a substantial reduction in the moment of inertia, and hence, a rapid increase in angular velocity. If the initial rotation rate should be near the instability limit, the sudden increase may cause profound effects. Is it possible that the resultant interaction could be such that the atmosphere is disrupted and escapes, carrying most of the angular momentum of the system, whilst the remainder of the earth is slowed down?

The moon, with only one-fifteenth the mass of the primitive atmosphere could be regarded as a product of the same cataclysm. This, of course, is the ancient fission hypothesis, which was discarded principally because of the angular momentum difficulty. If, however, most of the angular momentum is carried off by the escaping atmosphere this difficulty is relieved. Although such a process might seem far fetched, there is one powerful argument which should not be ignored because of its antiquity. The density of the moon (3·33 g/cm^3) is similar to the probable density of the earth's outer mantle. This correspondence must be regarded as significant empirical evidence supporting an origin by fission from the mantle, *after* the core had formed. The density of the moon is appreciably lower than that of oxidized earth or meteoritic material, and needs an admixture of water and other low density volatiles if it is to be regarded as forming separately in the same dust cloud, and close to the earth (Ringwood, 1959). Although this hypothesis is quite acceptable, it requires that the equality in density between the moon and mantle is nothing but a coincidence. One wonders.

For many years the angular momentum problem has perplexed students of solar system and stellar evolution. It now appears that a solution may be in sight.

This requires that angular momentum be transferred from a central star to a gaseous nebula or to ejected matter by means of magnetohydrodynamic interaction. Observational data on T-Tauri and related stars provide vital data, not yet fully understood. These stars, which are still in the Kelvin contraction stage, are observed to be ejecting large amounts of matter (Herbig, 1957). Some astronomers believe that this mechanism may be responsible for slowing down the angular velocity of the nucleus, whilst the escaping matter carries away most of the angular momentum. Whatever the details of the process may be, it is difficult to resist comparing the Kelvin stage contraction of such stars with that of the earth.

(f) *Special problems.* In a previous paper, the writer (Ringwood, 1959) discussed the densities and evolution of other planets, including Mercury. Some modification may be desirable. The density of Mercury is usually placed between 4·5 and 5·5 depending upon the radius, which is poorly known. It is not impossible that the density may be substantially lower than 4·5. If not, it demands a special process. If Mercury consists of highly-reduced solar non-volatile material of density 5 gm/cm^3 as previously suggested, about 2000 cal/g would be required for melting and reduction. This cannot be supplied by gravitational energy and it is difficult to account for it in terms of internal energy sources. It seems best to treat Mercury as a special case, owing to its proximity to the sun. When the sun was undergoing its Kelvin contraction, the temperature when it reached the radius of Mercury would be about 1000°K. Thus if Mercury grew out of material left behind as the sun contracted (Kuiper, 1957) it must have accreted at an initially *high* temperature (unlike other planets) and would therefore be highly reduced, and possess a high density (Ringwood, 1959).

A final remark on Mars. In the previous paper the writer suggested that Mars consisted of oxidized homogeneous non-volatile material. Although this suggestion is still feasible, the possibility is not excluded that Mars may possess a small amount of metal phase, either distributed homogeneously, or forming a core. Observational data are not yet precise enough to make a decision. It is certain, however, that there is much less metal present than in the earth.

5. *Cooling of the earth*

In part I, we concluded that the earth formed from a cold dust cloud, melted 4·55 aeons ago, and subsequently cooled to its present state. In the previous section it was suggested that melting and reduction were caused principally by gravitational energy. The problem to be considered in the present section is the mechanism by which the earth cooled from its molten to its present state.

For the earth as a whole to be cooling, it is necessary that the total rate of heat generation due to internal radioactivity should be less than the total surface heat flow. For many years, estimates of the radioactivity of meteorites indicated values too high for this condition to be attained. More recently, however, new techniques have shown that the amounts of uranium, thorium and potassium in metorites have been greatly overestimated. In a recent discussion, Birch (1958) has pointed out that the ratio

$$\frac{\text{total surface heat flow}}{\text{Mass of earth}}$$

is about equal to the latest estimates for rates of heat generation per unit mass in chondrites. If the earth had the same composition as chondrites, this would imply a state of approximate thermal equilibrium in the earth. When experimental uncertainties in the quantities involved are considered, it appears that there is no inconsistency in assuming that the earth contains meteoritic radioactive element abundances, and is, nevertheless, cooling.*

Cooling from the initial molten state will be controlled by convective and conductive processes. It will be convenient to consider these separately.

(a) *Cooling by convection.* JEFFREYS (1958) and others have pointed out that solidification of the earth's mantle from the molten state will occur from the base upwards, whilst the overlying liquid convects under the adiabatic temperature gradient, and radiates its heat away at the surface. Crystallization at the bottom, occurs because the melting gradient is much greater than the adiabatic gradient. If this process alone was involved the initial temperature gradient in the mantle after solidification would be the melting gradient as previously assumed. It is possible, however, that the basal crystal mush may undergo an independent convection, whilst the overlying liquid is still crystallizing and convecting (WAGER, 1958). This would greatly reduce the temperature throughout the solidified zone. There is some pertinent geochemical evidence relating to this possibility which will now be considered.

When thick basic intrusions cool very slowly, they usually display strong differentiation due to crystal fractionation. In a body the size of the mantle it would be expected that slow cooling and crystal fractionation would produce intense differentiation towards the surface. We have already noted that uranium, thorium and potassium display such a strong differentiation. However, petrologists have observed that the common rock-forming elements do not appear to have undergone strong differentiation. There is, for example, much less sialic rock material at the surface than would be anticipated. The absence of strong differentiation for this group of elements may be demonstrated by some examples.

Iron. A characteristic feature of the crystallization of magmas and artificial melts is the increase in FeO/MgO ratio as fractionation progresses. If fractional crystallization had affected the whole mantle, a strong enrichment of iron towards the surface would be anticipated. In fact, in minerals which are probably derived from there (olivines and pyroxenes in kimberlites and peridotites) the FeO/MgO ratio is usually less than 1/5, whilst the earliest olivines crystallizing from basaltic magmas usually have a similar ratio. If these minerals are characteristic of the upper mantle, it would indicate that the mantle has not been subjected to appreciable fractionation.

It might be suggested that there may be practically no FeO in the lower mantle

* Recent work by GAST (1958) indicates that the earth may contain only one-third as much rubidium as chondrites. GAST suggests that this deficiency may be due to a volatilization process which has operated during the formation of the earth, but not appreciably during meteorite formation. The accretion model developed in section 4(d) provides a satisfactory explanation. Rubidium would volatilize during the latter stages of formation of the earth, when dust was falling into the atmosphere and being reduced at a very high temperature.

If rubidium was lost by this mechanism, it would be accompanied by other elements which are volatile under similar conditions, e.g. potassium. If the earth contains only one-third as much potassium as chondrites it must be cooling.

and that therefore the low FeO/MgO ratio near the surface could represent a relative enrichment. However, the occurrence of oxidized nickel in appreciable quantities in the mantle (see next section) shows that such complete reduction of FeO is unlikely. Nickel is more noble than iron.

Nickel. The behaviour of nickel during crystallization of basic magmas is well known, e.g. Wager and Mitchell (1951). It becomes highly concentrated in the earliest ferromagnesians to separate, leading to impoverishment and virtual elimination from residual magmas. Accordingly if the mantle had undergone fractional crystallization it would be anticipated that negligible amounts of nickel should occur in the upper mantle. No such deficiency is observed in ferromagnesians from this region. Peridotites average about 0·3 per cent NiO (Ross *et al.*, 1954) whilst the olivines from basalts often contain similar amounts. Up to 0·45 per cent NiO occurs in kimberlites (Williams, 1932). The average amount of NiO occurring in chondrites is not well known. It is certainly below 0·25 per cent and probably below 0·1 per cent (Urey and Craig, 1953; Lovering, 1957).

Chromium. The behaviour of chromium during the crystallization of basic magmas is closely analogous to that of nickel. It enters early ferromagnesians in excess and rapidly becomes depleted, even virtually eliminated, from residual magmas (Wager and Mitchell, 1951). Peridotites and kimberlites usually contain around 0·2 to 0·3 per cent Cr_2O_3 (Rankama and Sahama, 1950, Ross *et al.*, 1954 Williams, 1932). Chondrites average 0·35 per cent Cr_2O_3 (Wiik, 1956). In view of the large scatter of analyses, there is no significant difference between these values. This again is an indication that crystal fractionation in ferromagnesian minerals has not operated appreciably in the mantle. Smaller quantities of Cr_2O_3 (0·03 — 0·05 per cent) found in basalts are consistent with an origin by fractional melting of chondritic material.

Formation of basalt. Bowen (1928) has pointed out that fractional melting of chondritic material would generate a basaltic magma, leaving residual peridotites. If however, the mantle had undergone appreciable differentiation by crystal fractionation early in its history, fractional melting of the upper part would not produce a basalt, but rather a more siliceous and alkaline product. Thus the ubiquitous formation of basaltic magma throughout space and time suggests that the outer mantle from which it is derived is dominantly of undifferentiated chondritic composition. (This of course assumes that basalt is produced by a partial melting process. It is difficult to conceive of a satisfactory alternative mechanism—complete melting of an eclogitic layer, for example, raises severe problems involving the supply of sufficient heat into highly-localized areas. There are also numerous other difficulties particularly of a petrological nature.)

The contrast in distribution between U, Th and K on the one hand, and Fe, Ni, Cr and probably most of the common elements, on the other, is most marked. The former group display extreme differentiation with intense upward concentration, whilst the latter are approximately uniformly distributed. The causes of this behaviour must be sought in the crystal chemical properties of the ions and the thermal history of the mantle.

The principal phases occurring in the mantle are probably olivines, pyroxenes, garnets and their high-pressure equivalents. It has already been noted that the

major elements which form these minerals do not appear to have differentiated, nor do the trace elements Ni and Cr, which are able to enter into solid solution in these phases. Strong differentiation is displayed only by the ions which are unable to enter, due to incompatible sizes and charges—U^{IV}, Th^{IV}, K^{I}. It is possible that ions such as Ba^{II}, Sr^{II}, Zr^{IV}, Pb^{II}, Cs^{I}, Tl^{I}, Rb^{I} also belong to this class. The fundamental difference in behaviour of these two groups in the mantle has been discussed in detail by Harris (1957).

The type of mechanism which appears most competent to explain the above distribution would be convection in the crystal mush during primary crystallization as suggested by Wager (1958). This would mix up and homogenize the major phases, whilst the small quantity of residual liquid containing ions unable to enter the major phases would be successively squeezed upwards, leading to strong concentration of U, Th and K near the surface.

Convection in the crystal mush would be driven by two factors.

(1) The earliest phases to crystallize at the base of the mantle are enriched in magnesium, and these become overlain by denser crystals increasingly rich in iron. Thus the normal tendency towards Fe–Mg fractionation must necessarily generate an unstable density distribution. This will lead to convective overturn, thereby mixing up phases and equilibrating the density distribution. The small amount of residual liquid greatly decreases the effective viscosity, and enhances convective overturn in the mush. There would probably be a critical depth of crystal mush required before convection takes place, and the rate of convection would be controlled by the rate of primary crystallization.

(2) The temperature gradient in the solidified region (melting gradient) is much higher than the adiabatic gradient and this will enhance the tendency to convect.

Convective overturns in the crystal mush as the mantle cools from the liquid state will cause rapid cooling throughout. The tendency will be to follow the adiabatic gradient. This phase of convective cooling in the crystal mush combined with upward concentration of U, Th, K etc., must have become complete 4·55 aeons ago, since the present uranium–lead ratio of the upper mantle was derived during the final stage of that process. It is not suggested that any further large-scale convective movements have subsequently affected the mantle, since the primary driving forces were only operative for a short time. Vening Meinesz (1944) and Wager (1958) have suggested that the location of primitive continental nuclei may have been due to such an early system of currents.

Nearly all of the cooling, required by the difference in curves I and II of Fig. 1 could be accounted for by a short period of convection which was completed 4·55 aeons ago. Subsequent conductive cooling would have been much slower.

(b) *Conductive cooling.* Most discussions of the earth's thermal history emphasize its high thermal inertia—cooling below 700 km by conduction is usually regarded as insignificant. However, these estimates depend critically upon the thermal conductivity assumed, and it now seems probable that this factor has been unduly minimized. Clark (1957) has pointed out that heat transfer in the mantle may be caused by radiation as well as normal lattice vibrations. Since this factor increases proportionally to the cube of the temperature and becomes significant around 1000°C it is likely to be of considerable importance. Clark suggested

that radiative conductivity would be of most importance in the earth above 600 km, since the increase of electrical conductivity with depth below this region would render it opaque to radiation. Recently however, Lawson and Jamieson (1958) have cast doubt upon this assumption and argued that radiative transfer is probably very important below 600 km. They estimate the total thermal conductivity of the lower mantle between 0·1 and 1·0 c.g.s. It could even be considerably higher.

If the initial temperatures in the mantle followed the melting gradient, it seems probable that thermal conductivities of this magnitude would cause deep and rapid cooling by conduction, irrespective of convection. The high melting temperature gradient would probably be unstable even if no convection occurred, and rapid heat transfer would occur, thereby keeping the outer mantle hot enough to transmit radiation. Subsequently, when the outer mantle cooled below 1000°C, radiative conductivity in this region would be inhibited. Once this stage was reached, cooling of the deep interior would proceed much more slowly, as at present.

Summarizing this section—the thermal history of the earth as determined from geochemical and geophysical data, requires that the earth cooled from a molten state to the present state. The cooling required is not incompatible with probable modes of heat transfer and generation within the earth.

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The uniformity of concentration of lithophile elements in chondrites—with particular reference to Cs

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Abstract—The paper is in two parts. In the first, the dispersion of concentration of the lithophile elements Li, Na, K, Rb, Mg, Ca, Sr, Ba, Al, Sc, Eu, Si, Ti, Zr, Th and U is examined in chondrites. Where twenty or more analyses have been made, relative deviations have been calculated; these range from 5 to 29 per cent. Some of the variation is clearly due to analytical error and it is concluded that the relative deviations of most, perhaps all, lithophile elements is near the lower limit (5 per cent) of the above range. Such small dispersion of concentration for a wide variety of elements, including Li, K and Mg which are sensitive to fractionation, indicates that chondrites have come from a source with an exceptionally uniform composition. It is concluded further that variation of concentration of a lithophile element in the silicate phase, as distinct from the meteorite as a whole, may be even smaller and that the ratio of one lithophile element to the other lithophile elements may turn out to be extremely small indeed. Analytical data of a very high order of excellence (relative deviation of 1–2 per cent) for all elements are evidently required to estimate such small variations precisely.

The second part of the paper is concerned specifically with caesium. This element has been estimated spectrochemically in K–Rb–Cs fractions obtained by ion exchange techniques from six chondrites and seven specimens of basic rock. In the chondrites, the Cs content (ave. 0·12 p.p.m.) and the K/Cs ratio (ave. 7000) remains constant to within the precision of the method of analysis. The magnitude of the average agrees with that (0·09 p.p.m.) of Webster, Morgan and Smales but the small variation of the Cs concentration and of the K/Cs ratio contrasts with their observations as they report large variations ($\times$ 30 or more). The K/Cs ratio in the seven basic rocks is fairly uniform (in contrast with granites) and similar in general magnitude to that in the chondrites.

Introduction

Chondrites are particularly important meteorites because they are abundant and have for some time served as important sources for estimating "solar system," "cosmic" and related abundances of the "non-volatile" elements (Goldschmidt, 1937; Suess and Urey, 1956, for example).

Several workers (see following discussion) have referred to the uniformity of the composition of the chondrites. The composition of these bodies is in certain respects much more uniform than that of specific terrestrial rock types, a conclusion which is becoming increasingly clear as the analytical data improve. The importance of the degree of uniformity of composition of chondrites has been stressed (Urey and Craig, 1953) particularly as a sensitive indicator of processes of differentiation and fractionation.

It will be recalled that the silicate phase content of the common chondrites does not vary very greatly (from 75 to 95 per cent) whereas the metal phase content varies by a factor of about 5 (5 to 25 per cent; see for example Fig. 1 of Urey and Craig, 1953). If therefore an element is strongly siderophile (the noble metals and nickel, for example) its concentration in chondrites may vary quite extensively; Fig. 4 of Urey and Craig (1953) which shows the distribution of nickel is a good example. Variation of concentration may be quite considerable if the element is only moderately siderophile and partly lithophile; see for example, Fe (the principal metal phase component) and Mn in Table 2 of Urey and Craig.

The lowest degree of variation is likely therefore to be found in the elements which are more or less distinctly confined to the abundant silicate phase. These include:

Group 1. Li, Na, K, Rb, Cs. Group 2. Be, Mg, Ca, Sr, Ba.
Group 3. B, Al, Y, rare earths. Group 4. Si, Ti, Zr, Th.

Some of these elements may not be entirely lithophile in chondrites. For example, calcium may occur in small amounts as oldhamite. Nevertheless, although small amounts of the lithophile elements may be present in the metal and sulphide phases, the magnitude of the distribution ratio

$$\frac{\text{concentration in silicate phase}}{\text{concentration in other phases}}$$

is usually so high that almost the entire lithophile element content is in the silicate phase.

In this paper we wish to assess the uniformity of concentration of several lithophile elements as quantitatively as possible. As certain siderophile or chalcophile elements (Fe for example) are present in the silicate phase in varying amounts we would wish to confine ourselves to examining the uniformity of composition of the lithophile elements in the "lithophile element fraction;" that is, the variation of concentration of the lithophile elements with respect to each other, but for the time being this is not possible.

The paper is in two parts. We wish first to consider sixteen lithophile elements and second to concentrate specifically on caesium, for which several new determinations (chondrites and basic rocks) will be given.

I. Variations of the Concentrations of Li, Na, K, Rb, Mg, Ca, Sr, Ba, Al, Sc, Si, Ti, Zr, Th and U in Chondrites

As early as 1878 Nordenskiold noted (Ahrens, 1957, with reference also to Wiik) that the Si and Mg contents of chondrites were quite strikingly uniform. Mounting evidence has since demonstrated that this holds for many lithophile elements, abundant and rare (Ahrens *et al.*, 1952; Urey and Craig, 1953; Pinson *et al.*, 1953; Ahrens, 1954a, 1957). The apparent existence (Brown and Patterson, 1947) of examples of extreme variation and of an inverse relationship between abundances of elements in silicate meteorites and the degree of variation of concentration has been shown to be almost certainly due to varying degrees of analytical error, some of which are gross (Ahrens, 1954b; 1957; see also Urey and Craig, 1953 and Fairbairn *et al.*, 1951, with regard to analytical error in silicate analysis).

Some analytical data are available on nearly all lithophile elements in chondrites. For our purpose, however, only certain data are usable. As we wish to assess the amount of dispersion of the concentration of these elements, it will be necessary in the first place to consider only those which have been estimated in a comparatively large number of samples. For statistical calculations twenty will be regarded as the minimum number. As dispersion of concentration is in any case small only data of seemingly high quality can be used, otherwise analytical

error is likely to be so excessive that its variation will be much greater than the natural variation of concentration.

Table 1 provides a summary of analytical data which have been selected together with estimated dispersion, expressed as relative deviation, on those

Table 1. Analytical data and statistical calculations on several lithophile elements in chondrites

Element	Average content	No. of samples analysed	Method of analysis	Dispersion (relative deviation) (%)	Source
Li	2·7 p.p.m.	21	spectrochemical	26	Pinson *et al.* (1953).
Na	0·7%	21 (but 2 discarded)	furnace distillation —flame photometer	5*	Based on the data of Edwards and Urey (1955); see also Fig. 5(a) of Ahrens (1957).
K(i)	0·09%	21	spectrochemical	27	Pinson *et al.* (1953) based on data of Ahrens *et al.* (1952).
(ii)	0·088%	21 (but 2 discarded)	furnace distillation —flame photometer	5*	Based on data of Edwards and Urey (1955) see also Fig. 6(a) of Ahrens (1957).
Rb	9 p.p.m.	21	spectrochemical	29	As for K(i)
Mg	23·8% (MgO)	94	chemical	7·3*	Ahrens (1957) based on data of Urey and Craig (1953).
Ca	2% (CaO)	94	chemical	24·6	
Sr	11 p.p.m.	21	spectrochemical	20	Pinson *et al.* (1953).
Ba	8 p.p.m.	21	spectrochemical	23	
Al	2·5% (Al_2O_3)	94	chemical	27·7	Ahrens (1957) based on data given by Urey and Craig (1953).
Sc	6 p.p.m.	21	spectrochemical	16	Pinson *et al.* (1953).
Si	38% (SiO_2)	94	chemical	7·2*	Ahrens (1957) based on data of Urey and Craig (1953).
Ti	0·11% (TiO_2)	21	spectrochemical	20–25	Based on data of Pinson (1954); see also Fig. 7 of Ahrens (1957).
Zr	33 p.p.m.	21	spectrochemical	23	Pinson *et al.* (1953).

* The relative deviations of these four elements are distinctly lower than the rest and may in fact approach the *true* relative deviation (no analytical error) for all, or nearly all, lithophile elements; see discussion in text.

lithophile elements which have been determined in twenty or more specimens of chondrite. For a few elements, the *magnitudes* given under "average" may be significantly in error. Rb is an example. Its concentration has been estimated spectrochemically in twenty-one chondrites. Dispersion is quite low (Table 1) but due to systematic error the given average value of 9 p.p.m. is evidently a little more than twice too high (see several papers listed by Ahrens, 1957). Sc, Sr, Ba and Zr are some other possible examples. The presence of systematic error does not, however, alter any of the conclusions arrived at here because we are

concerned primarily with the variation of concentration (dispersion) and not the magnitude of the concentration (abundance).

It is clear from Table 1 that the amount of variation for each element is very small (relative deviation <30 per cent). Dispersion may, however, be considerably smaller, for these reasons:

(i) It has been estimated (Pinson *et al.*, 1953; Ahrens, 1957) that about one-half of the dispersion of the spectrochemically determined values (relative deviations 16–29 per cent) for Li, K(i), Rb, Sr, Ba, Sc, Ti and Zr, is due to analytical error.

(ii) A considerable proportion of the dispersion of the chemically determined elements whose concentrations are fairly low (Al: ave = 2·5% Al_2O_3, relative deviation 27·7 per cent; Ca: ave = 2% CaO, relative deviation 24·6 per cent) is undoubtedly due to analytical error; observations on standard rocks G–1 and W–1 make this quite clear—see for example, Fairbairn *et al.*, (1951), and Table 1 and Figs. 1, 2 and 4 of Ahrens (1957).

(iii) Those elements which have been determined with the highest reproducibility (Si, at level of 38% SiO_2, and Mg, at level of 23·8% MgO (both determined chemically), and Na and K (both determined by furnace distillation–flame photometric procedures, Edwards and Urey, 1955; Edwards, 1955), show by far the smallest dispersion; for these four elements, the relative deviations fall within the range 5–7·5 per cent.

It is quite common to find that as the analytical accuracy is improved, the magnitude of dispersion of the concentration decreases quite sharply in chondrites. Potassium is a very good example. Thus, the relative deviation for this element in Urey and Craig's (1953) ninety-four selected analyses is at a magnitude of very roughly 100 per cent (these K estimations have been made mainly by means of the Lawrence Smith procedure which will almost certainly give grossly inaccurate results at a level of ~0·1 per cent), whereas for the twenty-one spectrochemical determinations (relative deviation of the spectrochemical method ~15–20 per cent) of Ahrens, *et al.*, (1952) the relative deviation drops to 27 per cent; for the highly reproducible (relative deviation ~3 per cent) furnace distillation–flame photometer determinations (twenty-one chondrites; two discarded) the relative deviation drops to a magnitude of only about 5 per cent.

It is not unlikely therefore that the relative deviations of all thirteen elements of Table 1 is ~5–10 per cent. The 95 per cent limits (relative deviation × 2) would therefore be 10–20 per cent. Variation of the composition of the silicate phase is presumably considerably less because of the fact that the Fe metal content of chondrites varies from 5 to 25 per cent (see Fig. 1, of Urey and Craig, 1953). The variation is not smooth (Urey and Craig, Fig. 1; Wiik, 1956) and although it is not possible specifically to correlate the metal variation with the estimated variation of the concentration of the lithophile elements it may be noted that the magnitude of variation of the total silicate phase (75 to 95 per cent; i.e. 85 ± 10 per cent) corresponds quite closely with the magnitude of dispersion (95 per cent limits = ±10–20 per cent). If therefore the small dispersion of concentration in chondrites as a whole is to some considerable extent due to variation in the total amount of silicate phase, the composition of the lithophile constituents

of the silicate phase of chondrites may be extremely uniform (relative deviation <5 per cent).*

Several recent determinations of rare lithophile elements in a comparatively small number of chondrites either support directly the dispersion data of Table 1 (Ba and Sc) or provide additional evidence (Eu, U and Th) for the generalization that, as a whole, the concentrations of lithophile elements vary only very slightly indeed in chondrites. Because only a few chondrites have been analysed, statistical calculations have not yet been attempted and the complete data have therefore been given (Table 2). Such small dispersion of concentration for a wide variety of

Table 2. Selected data (Sc, Eu, Ba, U and Th) in some chondrites

Meteorites	Concentration (p.p.m.)				
	Ba	Sc	Eu	Th	U
Modoc			0·08		(two related techniques)
	3·6	9·2	0·079	0·039	0·0108; 0·0108
Richardson		9·9	0·079		
	3·2	9·6	0·08	0·038	0·013; 0·0113
Forest City	3·7	8·9	0·073	0·0387	0·0099; 0·0106
Holbrook			0·081		
	4·0	9·7	0·081	0·038	0·014; 0·0112
Beardsley	—	9·2	0·074	0·0477*	—
Ave.	3·6	9·4	0·078	0·040	0·014

Ba and U (Hamaguchi *et al.*, 1957).
Th (Bate *et al.*, 1959).
Sc and Eu (Bate *et al.*, 1960).

* Bate *et al.* (1959) noted that aside from the Beardsley meteorite the Th content is virtually uniform. They point out that they used only 0·2 g quantities of meteorite for analysis and that variation of metal phase is therefore likely to cause a difference as the Th content in metal meteorites is extremely low.

elements, including Li, K and Mg each sensitive to certain processes of fractionation, indicates that chondrites have come from a source with an exceptionally uniform composition.

One seeming and contrasting exception to the above is caesium.

* Concerning the variation of concentration within the silicate phase alone we should recall that abundant iron plus some other non-lithophile elements will be present to some extent and that their variation will cause some variation in the total content of the lithophile elements in the silicate phase. If therefore the non-lithophile elements in the silicate phase are disregarded, it may turn out that the relationship between the different lithophile elements is very uniform indeed; that is to say, the ratio of the concentration of one lithophile element to that of the others would be almost constant, say to within 3–4 per cent. Such measurements are unfortunately not available. Spectrochemical methods could in principle be used because the spectra of many elements from a given specimen are recorded in a single spectrogram from which line intensity ratios (with respect, for example, to a silicon reference line) could be obtained. In order to be properly effective the reproducibility of the method would have to be quite unusually good; say, a relative deviation of 1–2 per cent. Such a reproducibility is unfortunately not yet attainable.

II. Variation of the Concentration of Cs in Chondrites and Some Basic Rocks

The caesium content of chondrites has recently been estimated by several workers (Cabell and Smales, 1957; Gordon *et al.*, 1957; Webster *et al.*, 1958) who used either neutron activation or mass-spectrometer–isotope-dilution techniques. Webster *et al.*, (1958) indicate that the comparatively high values of Gordon *et al.*, (1957) are evidently due to reagent impurities. Accordingly, we will disregard these values and consider only the neutron activation and isotope dilution values reported in columns (2) and (3) of Webster *et al.* Their range is large, i.e. 0·01 to 0·28 p.p.m. (twelve samples) a factor of more than $\times 30$.

Webster, *et al.* mention the possibility that leaching might sometimes cause low Cs but conclude that this is unlikely and that the large variation is probably real and is due to the geochemical character of Cs; in particular the fact that in feldspar the Cs content varies to a far larger extent than does Rb (Taylor and Heier, 1958, Heier and Taylor, 1959).*

If indeed, the large Cs variation is real, it is highly significant: either the chondrites have passed through some fractionation process which has affected Cs alone and not the other lithophile elements—some of which are highly sensitive to certain processes of fractionation (Li, K and Mg for example)—or if not, some other unknown agency has been the cause. Neither possibility seems likely and we have accordingly sought to verify the observations by Webster *et al.* For this purpose we have estimated Cs and the K/Cs ratio in six chondrites using an ion-exchange–spectrochemical procedure. For the sake of comparison we have also determined the K/Cs ratio in some specimens of basic rock.

Details of Analytical Procedure

A. *Ion exchange enrichment—chondrites*

Edge *et al.* (1959), Brooks, Ahrens and Taylor (1960), and Edge and Ahrens (in preparation) have discussed some of the applications of ion-exchange–spectrochemical procedures for the purpose of estimating trace elements in minerals, rocks, soils and meteorites. As the Cs concentration level ($\sim$0·1 p.p.m.) in chondrites is low, considerable enrichment must be achieved before a quantitative spectrochemical estimate can be attempted. Calculation shows that the principal constituents of chondrites, Si, Mg, Fe, Al, Ca and Na, have to be almost completely removed and it was therefore decided to attempt the spectrochemical determination in a potassium-rich fraction containing the two heavy alkali metals, Rb and Cs. For this purpose, the following four-step scheme (after sample dissolution and Si removal) was evolved:

(1) Removal of Fe (as chloro complex) on anion column.
(2) Removal of Al and some Mg and Ca through perchlorate decomposition and H_2O leach.

* This is certainly true also of granites where Cs (very large dispersion) contrasts sharply with Rb and K (moderate dispersion) (Ahrens, 1954a,b New England granite; Deleon and Ahrens, 1957, Yugoslav granites; Ahrens, 1959, and Edge and Ahrens, in preparation).

(3) Removal of Na (first cation exchange column).

(4) Removal of remaining Mg (second cation exchange column).

The scheme is therefore simple and involves the use of only a minimum number of reagents, namely: HF (40 per cent), HCl (s.g. 1·18), $HClO_4$ (60 per cent) and deionized H_2O. Spectrochemical tests on the purity of the liquid reagents and the resins (cation and anion) did not show detectable Cs. Volumes of reagents larger than those used in the actual analyses were taken to dryness and spectrochemically examined. The resins were examined by arcing the ash from 5 g of resin. Details are as follows.

Two separate 5 g samples of each chondrite powder (~ -150 mesh) were moistened with H_2O in Pt basins and treated with 15 ml $HClO_4$ and 20 ml HF. After slow evaporation 30 ml concentrated HCl were added to the dishes and warmed for 5 min during which period the contents of the dishes were stirred. The HCl was decanted into a 100 ml polythene bottle.

The residues were combined and treated with 15 ml $HClO_4$ and 10 ml HF and slowly taken to dryness. When cool, 20 ml concentrated HCl were added. The contents were warmed and stirred ($\sim$4 min) and decanted into the polythene bottle containing the first HCl decantation solution: 5 ml $HClO_4$ were added to the small residue in the Pt dish. Evaporation was continued until evolution of copious $HClO_4$ fumes had ceased. When the resultant residue was warmed only a very small dark residue remained: spectrochemical analysis showed this to contain only Fe and Cr and the residue was accordingly discarded. The HCl soluble fraction, together with a 2–3 ml wash of the Pt basin was added to the contents of the polythene bottle.

1. *Removal of* Fe—*use of anion column.* The HCl solution containing Fe as an anionic chloro complex was soaked into an Amberlite IRA–400 (8 ×, 100–200 #) anion exchanger in a 15 × 3 cm column at a flow rate of $\frac{1}{2}$ ml/min. Fe, as well as Co and Ti remained on the column while Li, Na, K, Rb, Cs: Mg, Ca, Sr, Ba; Al plus a few other rare elements appeared in the effluent; this was collected in a 600 ml beaker.

Before further use, absorbed Fe, Co and Ti were removed from the column by elution first with 200 ml 0·5 N HCl and then 100 ml deionized H_2O, both at a flow rate of 1 ml/min.

2. *Removal of* Al *and some* Mg *and* Ca—*thermal decomposition of perchlorates and* H_2O *leach.* The HCl effluent was evaporated to 40–50 ml and transferred to a silica 80 ml basin; two 10 ml washings (deionized H_2O) of the 600 ml beaker were added to the basin. Thereafter 10 ml $HClO_4$ were added and taken to dryness. The dried perchlorate residue was heated for 20 min at 550°C in an electric muffle, cooled and transferred to an agate mortar, ground and returned to the silica basin to which 50 ml of deionized H_2O were added and heated to almost boiling; when cool the aqueous extract was transferred to a 75 ml centrifuge tube and centrifuged. The supernatant liquor was poured into a 500 ml beaker and the residue was returned to the silica basin; the operation carried out seven times.

Spectrochemical analysis of the dried combined aqueous extracts showed the presence of Li, Na, K and Rb (Cs not detectable) plus, Mg, Ca, Sr and Ba. The leached residue (oxides) from the thermal decomposition of the perchlorates contained Al (presumably all Al), Mg, Ca, V, Ni, Cr and a very small trace indeed of Na (highly sensitive *D*-lines barely detectable); otherwise the alkali metals were not detectable.

3. *Removal of* Na—*use of the first cation column.* The aqueous extract residue was dissolved in 5 ml 1 N HCl. A 5 ml 1 N HCl wash of the 500 ml beaker was combined with the aqueous extract and absorbed on to cation exchanger Dowex 50 (8 ×, 200–400#) in a column 22 cm long and 1·9 cm diameter at a flow rate of 0·25 ml/min. 270 ml 1 N HCl was passed through the column at a flow rate of 25 ml/min. The effluent contained Li and Na but no detectable K, Rb or Cs and was discarded. Elution with 325 ml 2 N HCl was carried out and spectrochemical analysis of the dried effluent showed the presence of K, Rb, Cs (sometimes) with varying amounts of Mg and a little Ca. As Cs was only detected in those effluents which contained a minimum of Mg, this element was therefore removed in a final step.

The column may be regenerated as follows: 500 ml 6 N HCl were passed through the column at a flow rate of 30–35 ml/hr followed by 200 ml 1 N HCl at the same flow rate. Spectrochemical examination of the effluent residue showed the presence of Ca, Sr and Ba, but no alkali metals.

4. *Removal of remaining* Mg*—use of second ion exchange column.* The 2 N HCl effluent was evaporated to 20–30 ml and transferred, together with two 5 ml washings with deionized water, to an 80 ml silica basin and taken to dryness. 10 ml 3 N $HClO_4$ were added, warmed, and soaked into a 38 cm long $\times 1{\cdot}7$ cm diameter column of Dowex 50 (8 ×, 200–400#). The basin was washed out with warm 3 N $HClO_4$ and the washings were transferred to the column. When the liquid level in the chromatography tube had reached the resin surface, elution with 165 ml 3 N $HClO_4$ was commenced (flow rate 25 ml/hr). The effluent containing the heavy alkali metals was collected in a 250 ml beaker, taken to dryness and loaded into a graphite anode with a 5 mm cavity of 2·5 mm diameter. Qualitative examination of the spectra of these residues showed K as the dominant constituent and detectable Rb and Cs.

After elution with another 500 ml 3 N $HClO_4$ at the same flow rate as employed above, the column was again ready for use. Spectrochemical examination of the resultant residue showed the presence of Mg and Ca but no detectable heavy alkali metals.

Blank tests on the reagents which were carried through all the steps of the concentration procedure showed no detectable Cs 8521 or K 6911.

B. *Ion exchange enrichment—basic rocks*

As the Cs content of basic rocks was estimated to be about ten times greater then that of the chondrites it was not necessary to concentrate Cs as highly as above, and the following procedure was used.

After acid attack, as above, the dried residue was taken up with 2 N HCl and soaked into a 38 × 1·7 cm column of Dowex 50(8 ×, 200–400#) (flow rate, 0·25 ml/min). As soon as the liquid level reached the resin surface, elution with 260 ml 3 N HCl was commenced at a flow rate of 20 ml/hr. After 160 ml had passed through the column, the next 100 ml containing K, Rb, Cs and some Ca was collected in a 250 ml beaker. For Cs determinations in granite and syenite, a spectrochemical determination may be attempted on a dried residue for this solution, but in basic rocks it is necessary to remove most of the calcium. This may be achieved in a second column, thus. The effluent is taken to near dryness and soaked into Dowex 50 resin in a 22 × 1·9 cm column at a flow rate of 0·25 ml/min. The resin is eluted with 180 ml concentrated HCl at a flow rate of 25 ml/hr. The whole of the effluent is collected which when taken to dryness may be analysed spectrochemically. In order, however, to have the same matrices for basic rocks and chondrites we added 3 ml $HClO_4$ (60 per cent) to the almost-dry effluent after it had been transferred to an 80 ml silica basin. The silica dish was heated until fumes of $HClO_4$ ceased and the residue was then collected and arced as described below.

C. *Quantitative spectrochemical estimation of* Cs *and* K/Cs *ratios*

The K–Rb–Cs concentrate was loaded into $\frac{3}{16}$ in. National Carbon Co. regular grade graphite anodes (carbon upper electrode) and arced at 5 A. Exposures were superimposed where necessary. Spectra were recorded on Kodak 1–L plates. Care was taken to stop the exposure shortly before the whole sample was consumed because CN emission otherwise interferes excessively with Cs 8521, the analysis line. Background was nevertheless quite intense in several spectra and a particular effort was therefore made to estimate and correct for the presence of background. Cs 8521 was scanned on the microphotometer; Fig. 1 shows an example of such a microphotometer traverse. It is clear that background is not quite the same on either side of the line and correction required an extrapolation, as indicated on Fig. 1. For further details of the spectrochemical procedure see Edge (1960).

The standard diabase W–1 (Fairbairn *et al.*, 1951; see Ahrens and Fleisher, 1960, for recent review) served as a standard for Cs and for K. The Cs content that was used is that of Cabell and Smales (1957). Although the magnitude of the Cs contents of the chondrites will naturally depend therefore on the assumed magnitude of Cs and K in W–1, the amount of variation—the main object of this investigation –of Cs and of K/Cs on chondrites is independent of these magnitudes.

Discussion

1. Cs *and the* K/Cs *ratio in chondrites*

The estimated Cs content and ratio I Cs 8521/I K 6911 in six chondrites are given in Table 3.

Three conclusions are clear from Table 3. First, where direct comparisons of the Cs content are possible agreement may be either good (Limerick and Modoc) or very poor (Long Island and Bluff), and second, the Cs contents estimated here remain uniform whereas those of Webster *et al.* show extreme variation. The estimated Cs contents given here are based on the assumption that the K content of

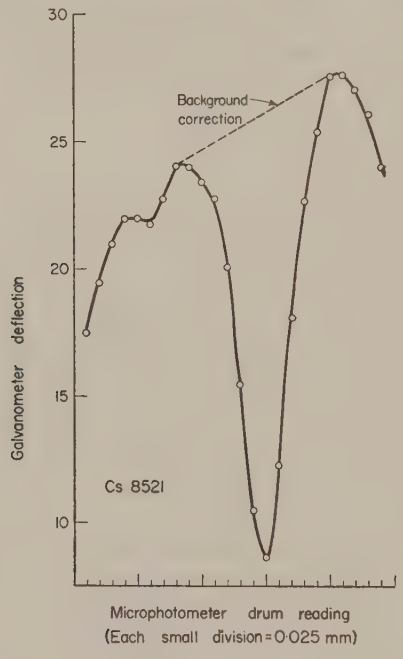

Fig. 1. Microphotometer traverse across Cs 8521 in K–Rb–Cs concentrate from a chondrite.

chondrites (ave = 850 p.p.m.) is constant, an assumption which seems reasonable in view of the observations of Ahrens *et al.*, (1952) and particularly Edwards and Urey (1955) and Edwards (1955). Though not completely independent, because they depend on the accuracy of the assumed K/Cs ratio in W–1, the Cs concentrations given here (ave 0·12 p.p.m.) may be taken to support the average value (0·09 p.p.m.) of Webster *et al.*, (1958). Third, to within the limits of experimental error, the K/Cs ratio remains uniform: this contrasts sharply with the observations of Webster *et al.* (see their Table 2) where K and Rb (one exception; Bluff) are fairly uniform but only Cs varies.*

* *Footnote added in galley.* Gast (1960) has estimated Cs (and Rb and K) in five chondrites and reports an average similar to that reported here and by Webster *et al.* (1958). The range of concentration (0·088 p.p.m. to 0·193 p.p.m.) is $\times 2$ and is a little greater than that given here (0·10 p.p.m. to 0·16 p.p.m. $= \times 1{\cdot}6$) but far less than that ($> \times 30$) reported by Webster *et al.* These comments apply also to the Cs/K ratio.

As only six chondrites have been analysed and because the determinations are not regarded as highly precise, it is not possible to make a rigorous statistical statement; nevertheless we may conclude—if the analyses given here are accepted —that the variation of Cs in chondrites must be quite small. Further work is, however, required in order to establish whether dispersion is as small as that of other lithophile elements discussed here.

2. *A comparison of the* K/Cs *ratio in chondrites and igneous rocks*

It is now well established that unlike K and Rb, the Cs content, and hence also K/Cs, varies over extreme ranges in granite (Ahrens, 1954a, b; 1959; Deleon and Ahrens, 1957; Edge and Ahrens, in preparation) and accordingly it

Table 3. Cs and (Cs 8521/K 6911) ratios in chondrites

Sample	$\frac{\text{I Cs 8521}}{\text{I K 6911}}$	Cs (p.p.m.)	
		This paper	Webster *et al.* (1958)
Limerick	0·19	0·11	0·10
Modoc	0·19	0·11	0·08
Long Island	0·25 *	0·18 *	
	0·20 †	0·13 †	0·01
	Ave. 0·23	Ave. 0·16	
Mangwendi	0·18	0·10	—
Dhurmsala	0·17	0·10	—
Bluff	0·21	0·14	0·01
			< 0·01
	Ave. 0·20	Ave. 0·12	

* 10 g.
† 20 g.
Average K/Cs ratio = 7000.

is difficult to arrive at an accurate estimate of the K/Cs ratio in granite which could be compared with the value in chondrites. Based mainly on the data of the above workers, the average K/Cs ratio will probably lie between 3000 and 9000, an order of magnitude which is similar to that in chondrites and in the basic rocks referred to in Table 4. It is likely that the K/Cs ratio in specific basic rocks is less variable than in granite, in which case it should be possible to estimate this ratio quite accurately: a comparison of the basic rock ratio with that of chondrites would be of considerable interest. Using the procedure outlined above, K/Cs ratios have been estimated in diabase W–1 (Fairbairn *et al.*, 1951) and six basic rocks from the Banks Peninsula, New Zealand; the results are given in Table 4.

Although the number of specimens is small (seven) and although most are from the same locality, the data are nevertheless instructive. In the first place,

the K/Cs does not vary greatly and secondly, the magnitude of the ratio is very similar to that estimated (7000, Table 3) for chondrites. Bearing in mind that the number of determinations is small we may conclude tentatively further, thus:

(i) As the ratio K/Cs does not seem to vary greatly in basic rocks, it is unlikely to vary greatly in chondrites, which supports the analytical data of chondrites in this paper and not those of Webster, *et al.* (1958).

Table 4. Cs/K intensity ratios, K/Cs concentration ratios an Cs contents of some basic rocks

Specimen* designation	Rock type	$\frac{\text{I Cs 8521}}{\text{I K 6911}}$	K (%)	Cs (p.p.m.)	K/Cs
W–1	diabase (dolerite)	0·35, 0·29 } 0·32	0·53	1·08	4900
T–83	basalt	0·26, 0·24 } 0·25	1·22	1·89	6500
T–100	basalt	0·18, 0·22 } 0·20	1·44	1·80	7800
T–101	basalt	0·20, 0·22 } 0·21	1·08	1·40	7800
T–112	olivine basalt	0·19, 0·19 } 0·19	0·75	0·89	8400
T–111	diabase (dolerite)	0·19 } 0·19	1·30	1·53	8500
T–86	gabbro	0·28, 0·28 } 0·28	0·26	0·46	5700
		Ave. 0·23			Ave. 7100

* See Appendix for further details on these specimens.

(ii) If the earth originated from chondritic substance, consolidation–differentiation processes did not significantly alter the K/Cs ratio. In this respect we may compare the K/Cs ratio with the K/Rb ratio. As far as can be ascertained, the ratio K/Rb in the common igneous rocks of the earth is more or less uniform and equal to that of chondrites and tektites (Ahrens *et al.*, 1952; Ahrens, 1954a, b; Taylor and Ahrens, 1959; Heier and Taylor, 1959).

The preliminary observations on the basic rocks discussed here indicate that the terrestrial K/Cs ratio may turn out to be equal to that in chondrites. If substantiated we will have two examples of pairs of elements whose terrestrial abundance ratio is equal to that of chondrites. As potassium is common to each ratio, the ratio K–Rb–Cs would be constant. Such information would provide strong chemical evidence in support of a common origin for earth and meteorites.

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Appendix

Notes on Basic Rocks from Akaroa, Banks Peninsula, New Zealand

	Map reference	Locality
T–83	N.Z.S. 94/256277	Duvauchelle Bay, road near wharf.
T–100	N.Z.S. 94/267289	Duvauchelle Bay quarry.
T–101	N.Z.S. 94/226273	Quarry, Barry's Bay–Hilltop Road, 600 ft above sea level.
T–112	N.Z.S. 94/209299	Quarry on Summit Road near Hilltop.
T–111	N.Z.S. 94/241262	French Farm quarry.
T–86	N.Z.S. 94/256263	East of Ohawe Peninsula.

T–86 is from a small gabbro intrusion exposed at the bottom of the caldera. T–83, T–100 and T–111 are early basalt flows, possibly unconnected with the main dome-building phase. T–101 and T–112 are basalt flows from the Akaroa basalt dome; T–101 is from an early flow and T–112 from one of the last flows.

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Deuterium abundance of natural waters

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Abstract—The deuterium abundance of natural water of various sources has been determined by the use of a deuterium mass spectrometer. The absolute deuterium contents of the reference sample nos. 1 and 1a of the U.S. National Bureau of Standards were found to be 0·0149 and 0·0128 mole % D_2O, respectively, by the comparison of the samples with the standard samples of known deuterium content. Relative enrichment of no. 1a to no. 1 $(R_{1a} - R_1)/R_1 \times 100$ was $14{\cdot}13 \pm 0{\cdot}23$, which agrees perfectly to the value reported by Craig. The variation of deuterium contents of tap waters of Tokyo and Osaka during last 2 years were within ± 1 per cent and any seasonal regularities could not be detected. Marine waters of the West Pacific have almost the same deuterium content as those of the Pacific coast of the United States. Marine waters at various depths of the Antarctic showed relatively large variation of deuterium content (from $+0{\cdot}84$ to $-1{\cdot}16$ per cent on the SMOW-scale), whereas the samples of Black Current of the Pacific showed little variation. It was found that the deuterium content of spring water suggests the origin of springs in some cases.

Introduction

Deuterium is one of the most interesting isotopes geochemically, because the deuterium content in natural water is greatly influenced by the history of the water samples: for example, the deuterium content of surface water is lower by about 5 per cent than those of marine water, due to the repeated vaporization and condensation. There are many reports on the differences in density of various natural waters, but unfortunately the difference in density was due to the variations in both deuterium and heavy oxygen abundances. Recently, the deuterium and heavy oxygen contents of natural waters have been measured mass-spectrometrically. The accuracy of the mass-spectrometric method is better than 0·5 per cent of the ratio of deuterium and protium in water of normal deuterium abundance, and this is accurate enough to discuss the history of water.

The deuterium abundance of natural waters was generally expressed by the percentage deviation from the working standards of which deuterium content is only an arbitrary one, and it is impossible to compare directly the data of the author with those of others, although conclusions of the author could be applicable to other cases. But the determination of absolute deuterium content and relative enrichment of Reference Samples of Isotope Abundances of U.S. National Bureau of Standards, 1 and 1a, will make it possible to compare precisely the deuterium content of working standards which was used in many laboratories. Also the deuterium content expressed on the SMOW-scale suggested by Craig will enable us to compare many data of different laboratories directly. In this paper, the writers express the deuterium content of natural water on SMOW-scale.

Experimental

Sample preparation

The apparatus used for the preparation of the hydrogen gas from water samples by reduction with hot zinc is shown in Fig. 1. About 20 mg sample of water

to be analysed was placed in vessel V (8 mm outer diameter and 10 cm long) by the use of a capillary pipette. The vessel was connected to the zinc reaction vessel by means of a ground joint. The zinc reaction vessel contained about 5 g of 30-mesh zinc dust which was prepared by turning a zinc stick with a lathe, and the temperature of the zinc dust was kept at 395 $\pm$ 1°C. The zinc reaction vessel, U-tube and Toepler pump were evacuated with a mercury diffusion pump for about 1 hr. After the sample of water in vessel V had been outgassed twice by repeated freezing and thawing and the Toepler pump isolated from the zinc reaction vessel with

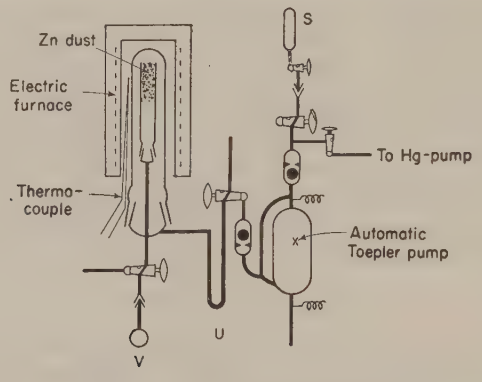

Fig. 1. Conversion apparatus.

a stopcock, the vessel V was allowed to warm up to room temperature. The water vapour, gradually evaporated, reacted with zinc to form hydrogen gas, and after 15 min the U-tube was cooled with liquid nitrogen and the hydrogen gas was pumped by means of the automatic Toepler pump into a sample tube S. In 1 hr all the water was converted to hydrogen and no water condensate could be detected in the U-tube. Care was taken to convert all the water sample to hydrogen gas and to compress it completely into the sample tube S.

About 100 ml of hydrogen gas of working standard was prepared from the Tokyo tap water in the same way as the sample gas. About 20 l. of the Tokyo tap water was collected on the 17 May 1957 at the Tokyo Metropolitan University as a working standard.

The deuterium mass spectrometer

A deuterium mass spectrometer used for the determination of D/H ratio of water samples was similar to the one described by Kirshenbaum (1951). Two collectors are used in a 2 in. 60° all-glass spectrometer tube. Accelerating voltage for hydrogen ions is 800 V, and the voltage on the electrode in the ion source is 27 V positive in respect to the accelerating electrode (= 800 V), and this voltage is very effective to minimize the formation of H_3^+ ions. No source magnet is used to avoid the discrimination effect in the ion source. Total filament emission current is adjusted to 3 mA, and the electron trap current is approximately 80 μA. Voltage applied to two focus-plates is adjusted to keep mass-2 ion current maximum. The voltages developed by the mass-2 and -3 ion beam currents

flowing through $2 \times 10^8\ \Omega$ and $5 \times 10^{10}\ \Omega$ resistors, respectively, are amplified by d.c. amplifiers and these two voltages are compared by means of a potentiometric method. Both mass-3 and mass-2 ion current are constant even when the accelerating voltage changes more than 50 V, and the slight change of accelerating voltage in this range has no effects on the D/H ratios.

The H_3^+ ion was corrected for by plotting (mass-3)/(mass-2) ratio as a function of H_2^+ which is proportional to gas pressure, and the extrapolating to zero H_2^+ ion currents (zero pressure). In practice, ratio dial reading of the potentiometer

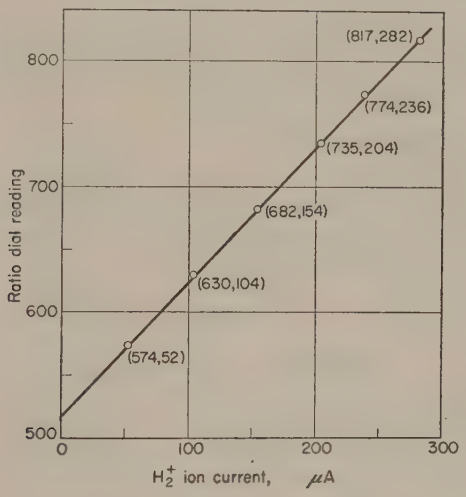

Fig. 2. Ratio vs. H_2^+ curve.

was plotted against H_2^+ ion current. Measured H_2^+ ion current ranged from 300 mV to 3 V across $2 \times 10^8\ \Omega$, and in this range of H_2^+ ion currents, the pressure curve gave quite a straight line, as is shown in Fig. 2. Maximum ion current in the spectrometer tube was about $1{\cdot}5 \times 10^{-8}$ A. In our mass spectrometer tube, ratio dial reading vs. H_2^+ ion current curve (pressure curve) did not give a straight line when the ion current was lower than 1×10^{-9} A. This may be due to the fact that the formation of H_3^+ does not follow the second-order reaction at a very low pressure. As the ratio dial reading obtained by extrapolating to zero H^{2+} ion current gives the ratio of HD^+ to H_2^+, the deuterium concentration of a sample was determined by comparing its ratio with that of the sample of known deuterium content (usually Tokyo tap water was used as a working standard). The order of analyses on the deuterium mass spectrometer was the working standard, a sample, the same sample, and the working standard. The variation of ratio dial reading of the working standard in a day was usually within $\pm 0{\cdot}5$ per cent.

Preparation of Standards

Preparation of heavy water

A sample of 99·6 D_2O mole % heavy water, which was kindly presented by Asahi Chemical Industry Co., was electrolysed to one-fifth of its original volume. The heavy water remained unelectrolysed was expected to have the concentration

of more than 99·9 mole % D_2O. The heavy water thus obtained was again electrolysed in a electrolytic cell of U-tube type, and the deuterium gas evolved was combined with the air oxygen on the heated copper oxide. The amount of air oxygen used was not enough to convert all the deuterium gas to heavy water. Thus, the oxygen isotopic content of the heavy water was the same as that of the oxygen in air. The heavy water was purified by Dole's method (1949), and its specific gravity was measured with the precision pycnometers of 30 ml capacity similar to those used by Kirshenbaum (1951), and its mole % was calculated by the following equation:

$$D_2O \text{ mole } \% = (924{\cdot}64 \times \Delta S)/(1 - 0{\cdot}0328\ \Delta S)$$

where $$\Delta S = S - 0{\cdot}999984$$

S is the specific gravity of the sample.

Heavy water from Norsk Hydro in Norway (99·77 wt. %) was also electrolysed in a electrolytic cell of U-tube type to make its heavy oxygen content the same as that of air oxygen. Thus, two heavy waters were used as the standard. In the following table is shown their deuterium content.

Sample no.	D_2O (mole %)
I (From Asahi Chem.)	99·739
II (From Norsk Hydro.)	99·628

Preparation of light water

Light water was prepared by repeated fractional electrolysis. Tokyo tap water was alkalized with potassium carbonate and was electrolysed in the glass cells, nickel and steel being used as anode and cathode, respectively. The separation factor of electrolysis was about 10, and the hydrogen from the cells was burned with its own oxygen: excess oxygen was supplied from another electrolytic cell. (1/6) → (1/2) → (1/2) in Table 1 has the following meaning. One-sixth of the Tokyo

Table 1. Light water

Sample no.	D_2O (mole %)	Method of preparation
A	0·0004 ± 0·00004	(1/6) → (1/2) → (1/2)
B	0·0002 ± 0·00004	(1/5) → (1/2) → (1/2)

tap water (about 3·3 l.) was electrolysed and the off hydrogen was converted to water. The water was again alkalized with potassium carbonate and was re-electrolyzed to one-half of its original volume. The process of re-electrolysis to one-half of its original volume was again repeated. Two samples of light water were obtained, and their deuterium content, determined mass spectrometrically, is shown in Table 1.

Preparation of standards

The intermediate standards containing from 0·78 to 1·09 mole % deuterium were made by diluting 0·5 g heavy water with 50 g distilled Tokyo tap water. The dilution data for the intermediate standards are summarized in Table 2. In the second and third columns of Table 2, is shown the deuterium content of the intermediate standards calculated from dilution data. "Ratio dial reading" is the readings of decade resister of the potentiometer when the hydrogen gas prepared by the zinc method from the intermediate standards was measured with the mass

Table 2. Intermediate standards

Sample no.	Deuterium content of standards (calculated from diln. data)		Ratio dial reading	Heavy water used in dilution		Distilled water (g)
	(mole %)	$(HD)/(H_2)_{calcd.}$	$(HD)/(H_2)_{calcd.} \times 10^{-2}$	Sample no.	Weight (g)	
1	0·9504	0·01919	196·3	I	0·46622	49·3408
2	0·6884	0·01386	180·8	I	0·34632	45·8398
3	1·0915	0·02207	180·6	I	0·60337	49·7499
4	0·8096	0·01632	179·2	II	0·42902	48·4100
6	0·8962	0·01809	180·7	II	0·47506	47·8956
7	0·7759	0·01564	181·0	II	0·42550	49·7469

Table 3. The normal standards

Standard no.	Deuterium content of the normal standards		Ratio dial reading	Intermediate standards used		Light water used	
	D_2O (mole %)	$(HD)/(H_2)_{calcd.} \times 10^2$	$(HD)/(H_2)_{calcd.} \times 10^{-4}$	Sample no.	Weight (g)	Sample no.	Weight (g)
8	0·0149	2·98	189	6	0·36972	B	22·11393
9	0·0139	2·78	188	3	0·29702	B	23·38067
10	0·0168	3·36	188	4	0·49699	A	24·04695
11	0·0153	3·06	$187._5$	3	0·38222	A	27·62422
12	0·0109	2·18	189	2	0·43923	B	27·87861

* These values were calculated from dilution data.

spectrometer. The ratios of (ratio dial reading) to $(HD)/(H_2)_{calcd.}$ must be constant in any concentrations (and this is true except for the sample no. 1), if there are no errors in the process of dilution. The sample nos. 2, 3, 4, 6 and 7 were then accepted as the intermediate standard. The intermediate standards were then diluted with light water to make the normal standard waters. The dilution data and the deuterium contents of five normal standards are given in Table 3. These normal standards were examined by taking the ratio of (ratio dial reading) to $(HD)/(H_2)_{calcd.}$ to avoid the error by dilution. The ratios were constant within the experimental error, and these samples (nos. 8, 9, 10, 11 and 12) were accepted as the normal standards.

Working standard

The Tokyo tap water, which was collected on 17 May 1957, was used as a working standard. Every 20 mg of standard samples and 100 mg of the Tokyo tap water were converted to hydrogen gas by the zinc method. The deuterium content

of the hydrogen gas from the various normal standards was compared with the deuterium content of the hydrogen gas from the Tokyo tap water on the deuterium mass spectrometer by plotting pressure curves and comparing the extrapolated intercepts. The comparison was made in the following order: Tokyo tap water (twice), normal standard (twice), Tokyo tap water (twice). The deuterium content of the Tokyo tap water was calculated by the following formula.

$$\text{D content of the Tokyo tap water (working standard)} = \frac{\text{(intercept with gas from the Tokyo tap water)}}{\text{(intercept with gas from normal standards)}} \times \text{(D content of normal standard)}$$

The results were shown in Table 4.

Table 4. Deuterium content of the Tokyo tap water (working standard)

Standard used for comparison		Total no. of M.S. analysis	Deuterium content of Tokyo tap water
Sample no.	D content (mole %)		
8	0·0149	8	$0{\cdot}0148_7 \pm 0{\cdot}00006$*
9	0·0139	6	$0{\cdot}0149_0 \pm 0{\cdot}00008$
10	0·0169	5	$0{\cdot}0149_5 \pm 0{\cdot}00008$
11	0·0153	5	$0{\cdot}0149_2 \pm 0{\cdot}00003$
12	0·0109	9	$0{\cdot}0148_2 \pm 0{\cdot}00008$
average			$0{\cdot}0148_9 \pm 0{\cdot}00005$†

* Average deviation.
† Probable error.

Results and Discussion

Reference samples of isotopic abundance of the U.S. National Bureau of Standards

Every 20 mg of eight aliquots of reference sample of isotopic abundance of the U.S. National Bureau of Standards nos. 1 and 1a were converted to hydrogen and their deuterium content was compared with that of working standard (Tokyo tap water). The percentage deviations of deuterium content relative to our working standard are shown in Table 5, together with their deuterium concentration

Table 5. Deuterium content of NBS-1 and -1a

Sample no.	δD(%) vs. Tokyo tap water	Absolute deuterium content (%)	SMOW-scale
NBS-1	$+0{\cdot}21 \pm 0{\cdot}16$*	$0{\cdot}0149 \pm 0{\cdot}0001$*	−4·76
NBS-1a	$-13{\cdot}95 \pm 0{\cdot}12$	$0{\cdot}0128 \pm 0{\cdot}0001$	−18·22

* Probable error.

calculated from the percentage deviation and the deuterium concentration of our working standard. Also in the fourth column, is shown the value expressed by the SMOW-scale suggested by CRAIG (1959).*

CRAIG (1959) pointed out that the relative enrichment of NBS-1a to NBS-1 $[(R_{1a} - R_1)/R_1 \times 100]$ measured by him and by the writers, are as follows:

Craig	the writers
$-14{\cdot}25 \pm 0{\cdot}25$	$-14{\cdot}13 \pm 0{\cdot}23$

The numbers agree perfectly within the uncertainties indicated. FRIEDMAN (1958) gave $-15{\cdot}33$, which is a little larger than ours, but the reason for the discrepancy is not clear.

Seasonal fluctuation in deuterium content of tap water

Tap waters are usually used as working standards for the measurement of the deuterium and heavy oxygen content of natural water (MORITA and TITANI, 1936, 1938; BAERTSCHI, 1953; FRIEDMAN, 1953; KIRSHENBAUM, 1951). But the deuterium contents of tap water of various places are somewhat different to each other, and the use of tap water as a standard is only an arbitrary one. Moreover their deuterium contents show random seasonal fluctuation. In Table 6 are shown deuterium contents of tap water of Tokyo and of Osaka city during the last 2 years. The data show that there is no relation between deuterium content and season and that the deuterium concentrations are consistent with each other $\pm$ 1 per cent (about $\pm 0{\cdot}15\ \gamma$) on the SMOW-scale. It was also found that the deuterium content of Osaka tap water was always slightly larger than that of Tokyo tap water. This may be due to the fact that the Osaka tap water stays a fairly long time in Lake Biwa before it runs down to Osaka, and during that time some enrichment of deuterium results by evaporation.

Ocean water

(a) *Surface water.* The surface water samples of the West Pacific, the Antarctic and the Indian Ocean were measured. The results are summarized in Table 7. As was pointed out by FRIEDMAN (1953), it was found that the deuterium content of marine water in frigid zone is slightly less than that in equatorial region. For

* CRAIG proposed to express deuterium content of natural water by the deviation from that of the STANDARD MEAN OCEAN WATER (SMOW). Deuterium content of SMOW is simply the average deuterium content of marine water samples analyzed for heavy oxygen by EPSTEIN and MAYEDA (1953). Although SMOW does not actually exist as a water sample and deuterium content of a sample can not be compared directly with that of SMOW, deuterium content of SMOW is exactly + 5·0 per cent higher than that of NBS-1 (CRAIG, H. private communication).
That is,

$$\frac{R_S - R_N}{R_N} = 0{\cdot}050 \qquad (1)$$

and from Table 5,

$$\frac{R_N - R_T}{R_T} = 0{\cdot}0021 \qquad (2)$$

where, R_S, R_N and R_T represent the deuterium content of SMOW, NBS-1 and the Tokyo tap water, respectively. From equation (1) and (2), deuterium content of NBS-1 on the SMOW-scale $((R_N - R_S)/R_S \times 100)$ is $-4{\cdot}76$ per cent, and that of Tokyo tap water $((R_T - R_S)/R_S \times 100)$ is $-4{\cdot}96$ per cent.

example, marine water off east coast of Mindanao and of the Indian Ocean has the deuterium content ranging from −0·1 to +0·5 per cent, but the deuterium content of the Antarctic and off south coast of Aleutian Islands lies between −0·7 to −1·4 per cent on the SMOW-scale. This fact must be due to the more rapid loss of light hydrogen during evaporation in equatorial region than in frigid zone.

Table 6. Seasonal fluctuation in deuterium contents of tap water

Date	δD(%) on the SMOW-scale	
	Tokyo tap water	Osaka tap water
April 1957	−4·5	−5·6
May	−5·0	−4·3
June	−5·4	−4·1
July	−5·4	−4·8
Aug.	−4·5	−4·3
Sept.	−5·8	−5·4
Oct.	−4·8	−4·2
Nov.	−5·0	−4·4
Dec.	−4·8	−4·9
Jan. 1958	−5·2	—
Feb.	−5·1	−5·4
Mar.	−5·5	−4·4
April	−4·4	−4·3
May	−5·2	−4·5
June	−5·3	−4·7
July	−5·5	−5·1
Aug.	—	−5·2
Sept.	−4·9	−4·2
Oct.	−5·3	−4·2
Nov.	−5·0	−4·5
Dec.	−5·0	−4·2
Jan. 1959	−5·4	−4·2
Feb.	−5·0	−4·4

The deuterium content near St. Lawrence is an exception and is surprisingly high, but the datum is a preliminary one and it will be necessary to know more about the deuterium content of ice and marine water around St. Lawrence for the clear explanation of this fact. Marine water off east coast of Japan shows the deuterium content ranging from −0·7 to +0·5 per cent. It is interesting that although the deuterium content of marine water on 36° north latitude ranges between +0·5 and +0·2 per cent, that on 38° north latitude ranges between 0 and −0·7 per cent on the SMOW-scale. Samples from Black Current of the Pacific shows the deuterium content between +0·2 and −1·2 per cent and has a tendency of decreasing the deuterium content near the east coast of Japan. This may be due to the effect of water from land.

(b) *Deep water*. Deuterium content of deep water at some points are shown in Tables 7 and 8. Deep water is somewhat lighter than surface water near the St. Lawrence, probably due to the streaming down of the melt water from the

Table 7. Surface and deep water

Sample no. or station	Location			δD (%) on the SMOW-scale	Date of collection
	Lat.	Long.	Depth (m)		
Pacific					
c-57	N: 32°20′	E: 142°03′	0	−0·1	10 Nov., 1957
c-56	N: 32°50′	E: 141°48′	0	+0·3	
c-55	N: 33°18′	E: 141°30′	0	−0·2	
c-54	N: 33°41′	E: 141°10′	0	−0·8	11 Nov., 1957
c-53	N: 34°03′	E: 140°50′	0	−1·2	
Os-30*	N: 63°03·4′	W: 172°54′	0	+0·7	5 Aug., 1956
			60	−1·3	
Os-48	N: 47°38·2′	W: 176°20·8′	0	−1·4	16 Aug. 1956
			90	−0·7	
			1462	−1·5	
St. 2†	N: 38°04′	E: 145°50′	0	+0·2	7 Oct., 1957
St. 3	N: 37°58′	E: 148°01′	0	+0·2	8 Oct., 1957
St. 5-1	N: 38°00′	E: 152°01′	0	−0·2	16 Oct., 1957
St. 5-2			30	−0·4	
St. 5-3			400	−0·1	
St. 7	N: 38°01′	E: 156°06′	0	−0·6	17 Oct., 1957
St. 9	N: 38°59′	E: 159°45′	0	0·0	18 Oct., 1957
St. 11-1	N: 37°59′	E: 163°59′	0	−0·4	19 Oct., 1957
St. 11-2			40	−0·8	
St. 11-3			250	−0·2	
St. 14	N: 38°06′	E: 170°03′	0	−0·7	20 Oct., 1957
St. 15-2	N: 36°12′	E: 169°58′	30	−0·1	21 Oct., 1957
St. 15-3			250	+0·6	
St. 17	N: 36°27′	E: 166°14′	0	+0·4	22 Oct., 1957
St. 19	N: 35°48′	E: 161°50′	0	+0·3	23 Oct., 1957
St. 21	N: 36°01′	E: 157°53′	0	+0·5	24 Oct., 1957
St. 27-1	N: 35°55′	E: 146°07′	0	+0·2	6 Nov., 1957
St. 27-2			75	−0·4	
St. 27-3			400	−0·9	
E 102	N: 32°40′	E: 137°08′	800	−0·2	Feb. 1958, (collected by Dr. Saizyo)
			1000	−0·2	
			1200	+0·3	
			1500	−0·1	
			2000	0·0	
			3000	0·0	
E 104	N: 31°58′	E: 135°52′	2000	−0·5	
			3000	+0·1	
			4000	−0·3	
B-0	N: 37°46·4′	E: 143°07·6′	0	+0·1	20 June, 1958 (by the French Naval-FNRS-III)
B-1			200	+0·6	
B-2			600	0·0	
B-3			800	+0·4	
B-4			1000	+0·4	
B-5			2500	+0·5	
B-6			3000	+0·3	

Table 7. Surface and deep water—(*contd.*)

Sample no. or Station	Location			δD (%) on the SMOW-scale	Date of collection
	Lat.	Long.	Depth (m)		
*Off east coast of Mindanao**					
1	N: 15°05′	E: 125°06′	0	+0·6	11 Nov., 1956
2	N: 12°00′	E: 126°00′	0	+0·3	
3	N: 08°30′	E: 127°18′	0	+0·5	
4	N: 04°14′	E: 128°55′	0	+0·5	
Indian Ocean†					
6	S: 12°48′	E: 78°63·8′	0	+0·6	
7	S: 15°11′	E: 64°34·5′	0	+0·1	
13	S: 29°00·5′	E: 39°03′	0	+0·7	
14	S: 39°00′	E: 20°26·0	0	+0·3	
15	S: 06°25′	E: 73°11·0′	0	−0·1	
Antarctic‡					
9	S: 65°04′	E: 52°49·5′	0	−0·8	
10	S: 67°08′	E: 38°37·5′	0	−0·8	
11	S: 68°52·5′	E: 25°33·5′	0	−1·1	
12	S: 68°12′	E: 23°31′	0	0·0	
13	S: 59°10·5′	E: 27°05·0′	0	−1·2	

* Collected by the *Oshoro-Maru*.
† Collected by the *Takuyo-Maru*.
‡ The First Japanese Antarctic Research Expedition, 1956-1957.

Table 8. Deuterium contents of deep water in the Antarctic*
(δD % on the SMOW-scale)

Depth (m)	Location		
	S: 66°46′ N: 41°18′ (23 Dec., 1957)	S: 67°46′ N: 38°53·5′ (9 Jan., 1958)	S: 68°32′ N: 36°30′ (9 Feb., 1958)
0	−0·7	−0·2	+0·9
10	+0·1	−0·7	−0·4
25	+0·3	+0·4	−1·0
50	−0·5	−0·9	+0·3
100	−0·5	−0·5	+0·3
150	−0·8	−0·5	−0·1
200	+0·4	−0·3	0·0
300	+0·5	+0·8	−0·1
400	+0·5	+0·1	0·0
500	−0·3	+0·1	+0·4
600	−0·6	+0·6	−0·3
800	+0·3	+0·3	−0·2
1000	+0·1	+0·1	
1200	+0·4	−0·3	
1500	−0·2		
2000	−0·3		

* Collected by the *Soya* (The Second Japanese Antarctic Research Expedition).

Arctic Ocean. On the other hand, no appreciable change in deuterium content could be observed in Black Current of the Pacific. Deep water in the Antarctic also shows appreciable variation of deuterium content ranging from +0·9 to −0·9 per cent on the SMOW-scale. This must be due to the streaming of current from various sources, that is, deep melt water, warm current from the Indian Ocean and surface melt water must be mixing quite irregularly.

Spring water

The writers measured about 230 samples of spring water and of ground water in Japan. The deuterium content of the spring water ranged from +1·0 to −10·0 on the SMOW-scale and about 70 per cent of it has the deuterium content from −3 to −7 on the SMOW-scale. In some cases, the deuterium content of spring water and of ground water can suggest some of its origin. For example, Ibusuki Spring (Kyushu, Japan), which is situated very near the sea, showed rather high deuterium content and it may be due to the mixing of marine water. On the other hand, samples of Beppu Spring (Kyushu, Japan), which is also very near the sea, have almost the same deuterium content as that of the surface water. This fact suggests that there occurs little mixing of marine water in Beppu Spring.

Ground water

The water of the gas well in Tiba and Kanagawa (Japan) has almost the same deuterium content as that of the marine water (from 0 to −0·9 on the SMOW-scale), but those in Niigata (Japan) ranges from −4 to −7 on the SMOW-scale. This fact suggests that the ground water is not necessarily of the same origin.

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The isotopic compositions and concentrations of lead in some chondritic stone meteorites*

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Abstract—Microgram quantities of lead were volatilized from the chondrites Richardton, Holbrook, Beardsley and Plainview and purified for mass spectrometric analysis. Aliquots of approximately 1 μg were surface-ionized by use of the boric acid technique. The isotopic compositions found range from highly radiogenic lead in the case of Richardton to leads in the other three chondrites which are substantially less radiogenic than average lead in the crust of the earth.

From our recent concentration determinations by the isotopic dilution method, it seems that the amount of lead in Beardsley is about 0·13 p.p.m. and that in Richardton about 0·06 p.p.m. The leads in these meteorites are consistent within a factor of approximately two with the lead–lead ages and the independently measured uranium and thorium concentrations. The lead–lead age for Richardton is the same as that found by Patterson (1955) for Nuevo Laredo, being 4·6 Æ||. The lead concentration measured for Forest City is 0·09 p.p.m., while that for Holbrook is 0·28 p.p.m. Holbrook is quite anomalous in containing 2·5 times the amount of radiogenic lead that can be explained by the accumulation of decay products *in situ* with a primeval lead which had the isotopic composition of the lead from the troilite in the Canyon Diablo and Henbury iron meteorites.

The total amount of lead on the surface of a meteorite appears to be comparable to the total amount inside. The isotopic composition of this surface lead indicates that it is principally terrestrial lead.

Introduction

The analysis of microgram quantities of lead has become increasingly important to cosmology and geochemistry. Because lead is the heaviest stable element, its concentration and distribution is especially significant for studies relating to the abundance of the elements and to the development of the planets. In particular, the isotopic composition and concentration of lead in meteorities may be related to the chemical evolution of the earth.

Lead–lead ages have been calculated from measurements of the isotopic composition of the lead in stone meteorites (Patterson, 1955; Marshall and Hess, 1958a). The ages found vary by no more than a few per cent from 4·5 aeons; they agree with independent determinations of the age of meteorites and of the earth. The validity of these lead–lead ages has been questioned because the concentration of lead and its isotopic composition in the stone meteorites require much greater amounts of uranium than have been observed directly (Patterson, 1955; Hamaguchi *et al.*, 1957). Although Edwards and Hess (1956) found somewhat less lead in the meteorites which they analysed, they could not conclude from the experiments that lower concentrations actually occurred. More recent experiments, suggested by these discrepancies, have shown that lower concentrations do occur in the meteorites (Marshall and Hess, 1958a).

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|| 1 aeon (Æ) = 10^9 years. This definition was introduced by Urey (1957).

For example, the concentration in the Forest City chondrite was found to be one-fourth that determined by PATTERSON (1955). A rather high concentration of lead and a considerable excess of radiogenic lead were found in Holbrook, however. At the same time, a much lower concentration was found for Richardton, another typical chondrite. Additional experiments are reported in the present paper and the data are more fully discussed.

EXPERIMENTAL PROCEDURE

Lead was separated from typical chondrites containing less than a part per million of that element. The process of volatilization followed by rapid chemical purification used for these experiments has been described in detail elsewhere (MARSHALL and HESS, 1960). Only a brief discussion of the experimental steps is given now, except for a description of the treatment of the fusion crust and all outer surfaces of the individual chondrites (see Appendix A). After the surfaces had been cleaned, dry pieces of the chondrites were crushed in a stainless steel mortar. Lead was then volatilized from the powdered chondrites in precleaned carbon crucibles by means of an induction heater; temperatures of 1300–1400°C were obtained by using quartz-glass heat shields surrounding the graphite crucibles. The condensate on the quartz-glass surface of the water-cooled jacket was rinsed out with nitric acid. Lead was quickly separated from the small quantities of other volatile constituents by means of the dithizone process. Concentrations were determined by the isotopic-dilution method. For this purpose, spike lead was added to the crucible and volatilized with the lead in the meteorite samples.

Samples of lead approximately 1 μg in size were placed on single tantalum filaments together with a little boric acid. Analyses were made with a single-focusing mass spectrometer with a 9 in. radius of curvature and a 90° deflexion. The filament temperature was controlled with a current-stabilizing circuit. The output of the electron multiplier was fed into a vibrating-reed electrometer, and the ion intensity was recorded on strip charts.

RESULTS

Concentrations of lead

Recent determinations of the concentrations of lead in seven stone meteorites are briefly summarized in Table 1. For three of these, the results determined in the present study are based on a number of individual analyses by the isotopic dilution method; these data are given in Table 2, Part I. Thus, the value for Richardton in the second column of Table 1 is the average of two analyses; that for Holbrook, six analyses; and that for Forest City, two analyses.

The individual values given in Table 2 are uncertain because of the blank correction, which amounts to $1{\cdot}5_3 \pm 0{\cdot}4_4$ μg of lead per volatilization. This correction represents from 23 per cent to 82 per cent of the total amount of lead observed in the concentration determinations. The uncertainty in the blank is large, around 30 per cent. For those meteorites with low concentrations of lead (Richardton, Forest City and Beardsley), the error in the concentration may be as much as 50 per cent. Nevertheless, the agreement of the present values with the independent neutron activation experiments of REED *et al.* (1958) and with our

Table 1. Concentrations of lead in stone meteorites

Meteorite	Amount of Pb (p.p.m.)				
	Present work	Reed *et al.* (1958)	Marshall and Hess (1958a)	Edwards and Hess (1956)	Patterson (1955)
Richardton	$0{\cdot}05_5$	—	$0{\cdot}1_1$*	—	—
Holbrook	0·28	0·38	0·32	0·28†	—
Forest City	$0{\cdot}09_0$	<0·15	0·095	—	0·4
Beardsley	0·13	0·15‡	—	—	—
Plainview	0·46	—	—	—	—
Modoc	—	<0·09	—	0·3	0·9
Nuevo Laredo	—	0·76§	—	—	0·7**

* Average of two isotopic dilution experiments.
† Average of five values for the amount of Pb recovered after volatilization from 15 g samples, each run corrected for 1 μg contamination.
‡ Recalculated on basis of the isotopic composition reported in this paper (Table 4).
§ Recalculated on basis of corrected values for the isotopic analysis by Edwards and Hess (1956),
** Reported as 0·68 p.p.m. by Reynolds and Lipson (1957).

Table 2. Quantities of lead observed for chondrites—I. Isotopic dilution experiments

Chondrites	Amount of sample (g)	Amount of Pb determined by isotopic dilution (μg)	Concentration of Pb (p.p.m.)*
Richardton	17·45	1·87	0·019
	11·56	2·58	0·091
Average Richardton			0·055
Holbrook-N	10·36	1·90	0·036
	10·04	3·50	0·32†
Holbrook-M 1	14·02	4·47	0·21
	10·31	6·77	0·51
Holbrook-M 2	9·41	6·15	0·49
	10·49	2·78	0·12
Average Holbrook			0·28
Forest City-1	10·57	2·51	0·093
Forest City-2	4·87	1·95	0·086
Average Forest City			0·090
Beardsley	9·48	2·78	0·13
Plainview	10·87	6·57	0·46

* Includes correction for $1{\cdot}5_3 \pm 0{\cdot}4_4$ μg of lead for each experiment.
† No quartz shield was used in this experiment. Blank correction was 0·25 μg of lead.

Table 2. Quantities of lead observed for chondrites—II Extractions of natural lead

Chondrite	Amount of sample (g)	Approximate colorimetric estimate of Pb recovered (μg)*	Concentration of Pb (p.p.m.)
Richardton (b)	75·5	4	$\geq$0·05
Holbrook-N (b)	41·5	~6	$\geq$0·14
Holbrook-M 1	102·3	20	$\geq$0·20
Holbrook-M 2	70·0	6†	>0·090
Beardsley	48·5	6	$\geq$0·12
Plainview	67·5	10	$\geq$0·15

* For some meteorites, the colorimetric estimate may be a little large because of partial destruction of the dithizone during the original extraction with the dilute standardized dithizone solution. This effect tends to compensate for the yields of the chemical extractions (which range from 30 to 80 per cent.)

† Re-extracted.

earlier isotopic dilution determinations (Marshall and Hess, 1958a) indicates that the blank correction is reasonably precise. Provided that sufficient material is available for analysis, the error due to the correction for contamination may be substantially reduced in any individual run by simply doubling the size of the samples used in the present experiments.

The amounts of lead recovered for the determinations of the isotopic composition of the lead in the chondrites were estimated colorimetrically. These amounts are listed in Table 2, Part II. With these estimates, approximate lower limits for the concentration of lead have been calculated and are given in the table. Most of the values agree within a factor of 2 with the more precise results from the isotopic dilution experiments on other aliquots of the same samples.

The amounts of contamination lead have been reduced considerably by the volatilization and simple chemical procedures used in these experiments. With 25 g samples and contamination at the level of about 1 μg of lead, it is possible to observe concentrations as low as 0·05 p.p.m. The concentrations found for Forest City and Modoc by Patterson (1955) and by Edwards and Hess (1956) were considerably higher than those observed in the present experiments and in those by neutron activation (cf. Table 1). This difference seems to be due to greater sensitivity of the more recent experiments, although different portions of the same meteorite may not have the same concentration of lead.

Isotopic compositions

From the concentrations of lead and with the assumption that all the contamination lead had been introduced in the volatilization step in these experiments, the observed isotopic compositions in Table 3 were corrected to those in Table 4. The precision of the mass spectrometric data in the current results was much greater than in our earlier experiments (Marshall and Hess, 1958a). With comparable amounts of lead used on the filament in our present experiments, the boric acid technique (Marshall and Hess, 1960) gave greater ionization efficiency and a more stable ion beam. In addition, with this procedure most of

Table 3. Observed isotopic ratios* of lead from chondrites, with standard errors of the mean and amounts of contamination

Chondrite	$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{206}}{Pb^{207}}$	$\frac{Pb^{206}}{Pb^{208}}$	Contamination (%)
Richardton (b)	38·16 ± 0·34 (31)†	1·3776 ± 0·0038 (37)	0·6782 ± 0·0016 (37)	$52_{.4}$
Holbrook-N (b)	20·69 ± 0·20 (37)	1·3517 ± 0·0059 (28)	0·5716 ± 0·0022 (28)	$20_{.6}$
Holbrook-M 1	16·98 ± 0·08 (10)	1·1557 ± 0·0057 (10)	0·4698 ± 0·0043 (10)	
	16·94 ± 0·12 (20)	1·1482 ± 0·0043 (24)	0·4693 ± 0·0017 (24)	
Average	16·96	1·1519	0·4695	$15_{.3}$
Holbrook-M 2	16·49 ± 0·28 (42)	1·152 ± 0·003 (144)	0·4758 ± 0·0012 (142)	$19_{.0}$
Beardsley	15·07 ± 0·12 (20)	1·1327 ± 0·0027 (46)	0·4462 ± 0·0011 (43)	$32_{.7}$
Plainview (a find)	15·30 ± 0·10 (39)	1·1057 ± 0·0039 (51)	0·4430 ± 0·0012 (50)	$12_{.9}$

* All isotopic ratios have been corrected by a factor to account for the relatively greater sensitivity of the multiplier to higher velocity ions (Inghram *et al.*, 1953). The correction is of the form

$$\frac{I_1}{I_2}\text{ corr.} = \frac{I_1}{I_2}\text{ meas.}\sqrt{\left(\frac{M_1}{M_2}\right)}$$

where I_1 and I_2 represent two ion intensities and M_1 and M_2 the masses of the ions, corresponding. The ions are assumed to be singly charged.

† ( ) designates number of ratios averaged.

Table 4. Isotopic compositions of lead in chondrites, corrected for contamination

Sample	$\frac{Pb^{206}}{Pb^{204}}$ (α)	$\frac{Pb^{207}}{Pb^{204}}$ (β)	$\frac{Pb^{208}}{Pb^{204}}$ (γ)
Richardton (b)*	>38·16	>27·70	>56·27
Holbrook-N (b)	$21{\cdot}2_0$	$15{\cdot}2_2$	$35{\cdot}5_3$
Holbrook-M 1	$16{\cdot}6_8$	$14{\cdot}5_7$	$35{\cdot}6_8$
Holbrook-M 2	$16{\cdot}0_4$	$14{\cdot}0_4$	$33{\cdot}8_2$
Beardsley	$13{\cdot}6_7$	$12{\cdot}4_0$	$31{\cdot}8_5$
Plainview	$14{\cdot}8_7$	$13{\cdot}6_1$	$34{\cdot}0_0$

* Because the lead from Richardton (b) is very radiogenic and because its concentration has a large uncertainty, the isotopic ratios given here have not been corrected for contamination. The ratios listed here are only lower limits of the actual ratios in the meteoritic lead. The uncertainty in the absolute values of the corrected ratios would be much greater than 34 per cent in this case.

the original sample could be retained conveniently for additional analyses. The data for the two aliquots of the lead isolated from Holbrook-M 1 (Table 3) illustrate the precision of the mass spectrometric measurements.

Correction for contamination involves two factors, namely: (a) the isotopic composition of the contamination lead; (b) the percentage contamination. Although the isotopic composition of the contamination lead is not known, generally this lead will have an α ($\equiv Pb^{206}/Pb^{204}$) between 18·5 and 19·0, β ($\equiv Pb^{207}/Pb^{204}$) between 15·5 and 15·7, and γ ($\equiv Pb^{208}/Pb^{204}$) between 38·5 and 39·5. Even values somewhat outside these limits will introduce little error into the correction. The principal uncertainty is in the percentage of contamination. This depends on the accuracy with which the blank and the concentration of lead in the meteorite are known.

The equation used in correcting the observed ratios in Table 3 to those in Table 4 was:

$$\alpha = \frac{\alpha_m - x(\Sigma_m/\Sigma_c)(A_m/A_c)\alpha_c}{1 - x(\Sigma_m/\Sigma_c)(A_m/A_c)}$$

(with expressions of similar form for β and γ), where $\Sigma = 1 + \alpha + \beta + \gamma$ and A is the atomic weight. The subscript m refers to the observed values; the subscript c, to the contamination lead. The fraction of contamination, x, is also given in Table 3. For contamination lead the isotopic compositions of 18·68, 15·64 and 38·73 were used for α, β and γ, respectively (the values for average modern crustal lead; Marshall, 1957).

The capacity of each crucible was about 25 g. For the isotopic composition of the lead in each chondrite, the acid rinses from successive volatilizations were combined into one solution (Table 2, Part II). The comparatively small amounts of reagents used probably added little extraneous lead directly (Marshall and Hess, 1960), but some contamination could enter during the further treatment of the solution. Because the contamination has been calculated on the basis of the average blank carried through the complete process multiplied by the number of volatilizations, the percentage contamination in the isotopic compositions (Table 3) may be somewhat overestimated. It should be noted that the quantity of any contamination lead added to the blanks after partial loss of the spike would also be overestimated.

The possible error introduced by all uncertainties seems to be about 3 per cent for most of the isotopic compositions given in Table 4. The more the isotopic composition of the lead in the sample differs from that of the contamination lead, the greater is the uncertainty in the corrected ratios α, β and γ, due to the uncertainty in estimating the fraction of contamination. However, calculations of lead–lead ages are little affected by these corrections, as can be seen by comparing the quantities calculated from the corrected compositions (Table 6) with those determined from the directly observed ratios (Appendix B).

All the chondrites in Table 4 are observed falls except Plainview. Although Holbrook-N was not gathered until about 25 years after its fall, the isotopic composition of its lead is rather similar to the analyses for the other two pieces of Holbrook (M 1 and M 2). The value in Table 1 for the concentration of lead in

this chondrite is an average from determinations on all three samples. The amount of lead may vary from one part of the meteorite to another (see following section on discussion of results); and this variation might account for the differences among the several isotopic analyses for the lead from Holbrook.

Holbrook, Beardsley and Plainview have lead which is considerably less radiogenic than typical terrestrial lead. The lead from Richardton is very radiogenic and comparable to that found by Patterson (1955) in Nuevo Laredo.

In earlier experiments on different portions of Richardton and Holbrook, the following isotopic ratios were observed:

Richardton (a)

$$\alpha = 26._{06} \begin{matrix} + 3{\cdot}2 \\ - 2{\cdot}8 \end{matrix} \qquad \beta = 21._{03} \qquad \gamma = 46._{84}$$

(8)

Holbrook–N (a)

$$\alpha = 17{\cdot}61 \pm 0{\cdot}07 \qquad \frac{Pb^{207}}{Pb^{206}} = 0{\cdot}887 \pm 0{\cdot}002$$

(94) (57)

$$\frac{Pb^{208}}{Pb^{206}} = 2{\cdot}210 \pm 0{\cdot}004$$

(57)

These average ratios have been corrected for discrimination by the electron multiplier (see footnote*, Table 3). Uncertainties are given as standard errors of the mean. It would probably be more accurate to consider the limits of possible error for these two analyses to be three times the standard errors of the mean. The number of ratios measured is given in parentheses. The ratios for Richardton (a) were corrected for $13._3$ per cent contamination, and those for Holbrook–N (a) were corrected for $7._5$ per cent contamination, to the following final values (Marshall and Hess, 1958a):

	α	β	γ
Richardton (a)	$27._{57}$	$22._{13}$	$48._{51}$
Holbrook–N (a)	$17{\cdot}5_2$	$15{\cdot}5_2$	$38{\cdot}9_3$

The uncertainty in the measurement of Pb^{204} in the isotopic analysis of Richardton (a) introduced a large possible error in α, β and γ. This sample was also left for some time in acid solution after the volatilization step and before final separation. Because more recent experiments (Chow and McKinney, 1958; Marshall and Hess, 1960) have indicated that contamination from the air may occur in acid solutions left for some time, the amount of contamination in Richardton (a) may have been underestimated. In spite of these uncertainties, a comparison of Richardton (a) with Richardton (b) (Table 4) still suggests that real differences in the isotopic composition of lead may occur from one part of the meteorite to another part.

For Holbrook, the approximate average value $\gamma = 35._7$ found by Reed *et al.* (1958) is in general agreement with the corresponding values in Table 4; and their value of $\gamma = 32._2$ for Beardsley agrees very well with the determination reported here. Their value of $\gamma = 51._4$ for Nuevo Laredo is in better agreement with that found by Edwards and Hess (1956), who observed the following: $\alpha = 34{\cdot}48$, $\beta = 25{\cdot}86$ and $\gamma = 52{\cdot}07$ (corrected for $11._6\%$* contamination: $\alpha = 37{\cdot}8_9$, $\beta = 28{\cdot}0_7$ and $\gamma = 54{\cdot}9_5$) than with the value found by Patterson (1955), who

* 1 μg of contamination lead is assumed for the 10 g of meteorite. A concentration of 0·76 p.p.m. (Reed *et al.*, 1958) is taken for this estimate.

reported $\alpha = 50{\cdot}28$, $\beta = 34{\cdot}86$ and $\gamma = 67{\cdot}97$. The lead concentration may be calculated by combining the analysis of EDWARDS and HESS (1956) with either the Pb^{204} or the Pb^{208} concentration found by REED *et al.* (1958). When the Pb^{204} value is used, the total lead is 0·78 p.p.m. Use of the Pb^{208} value gives a total lead of 0·74 p.p.m.

Stone meteorites evidently are good scavengers of lead, to judge from the

Table 5. The isotopic compositions* and amounts of lead leached from the surfaces of chondrites

Sample	$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{206}}{Pb^{207}}$	$\frac{Pb^{206}}{Pb^{208}}$	Amount of Pb recovered (μg) (colorimetric estimate)
Fusion crust of Holbrook-M 1:				
1st acid rinse	18·19 ± 0·27 (29)†	1·193 ± 0·004 (73)	0·5046 ± 0·0025 (73)	10
2nd acid rinse	16·61 ± 0·57 (5)	1·223 ± 0·010 (13)	0·5171 ± 0·0033 (13)	1
Surface of Plainview:				
1st leach	19·14 ± 0·05 (24)	1·209 ± 0·004 (28)	0·4961 ± 0·0018 (27)	15
2nd leach	$20{\cdot}9_6$ ± 2·8 (4)	1·223 ± 0·009 (33)	0·5185 ± 0·0041 (33)	10
3rd leach	16·83 ± 0·36 (22)	1·218 ± 0·004 (30)	0·5064 ± 0·0014 (30)	8
4th leach	17·97 ± 0·27 (16)	1·213 ± 0·006 (30)	0·5123 ± 0·0041 (29)	3
5th leach	—	—	—	0

* All isotopic ratios have been corrected for discrimination by the electron multiplier (see footnote* of Table 3).

† ( ) designates number of ratios averaged. Standard errors of the mean (standard deviation/$\sqrt{N}$) are given.

relatively large amounts observed on their surfaces. Table 5 gives the amounts and isotopic compositions of the lead recovered from the exteriors of Holbrook and Plainview. The first lead to be dissolved from the surface was principally terrestrial lead. This surface lead from Holbrook-M 1 had the following composition: $\alpha = 18{\cdot}19$, $\beta = 15{\cdot}25$, $\gamma = 36{\cdot}05$. The corresponding values for the lead from the exterior of Plainview were 19·14, 15·83 and 38·58. Subsequent acid washes contained more of the meteoritic lead, which was considerably less radiogenic in both of these chondrites (cf. the analyses in Table 5 with those in Table 4). The contamination lead appeared to be quite surficial.

Discussion of Results

Variations of concentrations and isotopic compositions in chondrites

In reporting additional analyses of stone meteorites, Wiik (1956) affirms the general conclusion that one chondrite is remarkably like another in composition. The percentages of any major constituent generally agree well within a factor of 2. Nearly all the sodium and potassium contents of the chondrites are within 25 per cent of the average (Edwards and Urey, 1955; Edwards, 1955). Even the trace elements rubidium, lithium, tin and scandium do not vary by more than about a factor of 2 in the group studied by Pinson *et al.* (1953). The uranium concentrations of a number of chondrites (Hamaguchi *et al.*, 1957; Reed, 1958) are all very close to 0·011 p.p.m.

However, not all of the trace elements are as uniformly distributed as the above analyses imply. Caesium concentrations in a dozen chondrites form a nearly continuous set of values from 0·01 to 0·28 p.p.m. (Webster *et al.*, 1958). Substantial variations in the bismuth content of chondrites may also occur (Reed *et al.*, 1958). Extreme values for the concentrations of the rarer, less refractory elements may differ by an order of magnitude. Thus, the variations in the amounts of lead in chondrites reported here (Table 1) is quite reasonable.

The chondrites are heterogeneous and represent agglomerations of material only a few microns to a few centimeters in diameter (cf. Urey, 1958). Therefore, the concentration of trace elements could be expected to vary considerably within a given stone meteorite. For example, a sample of Holbrook apparently contained 0·090 p.p.m. of thorium (Bate *et al.*, 1957) but another piece had the typical value of 0·038 p.p.m. (Bate *et al.*, 1959). Significant variations in concentrations would, however, be more likely to occur for the more easily fractionated elements. These would include, among the heavy elements in low abundance, mercury, thallium, caesium, bismuth and lead.

The concentrations presented in Table 2, as well as those from our earlier isotopic dilution experiments (Marshall and Hess, 1958a), vary by as much as a factor of 10 within the same meteorite. Errors in the estimation of the blanks may be partly responsible for this variation. For example, in the second determination for Holbrook-N (Table 2, Part I), the blank correction was rather small and the concentration is very close to the average value. In contrast, the concentration from the first determination of Holbrook-N would still be comparatively low if the blank correction were negligible. The concentration would be calculated too low if the spike lead were recovered but if some of the lead did not volatilize from the sample of meteorite. Because the average concentrations by the volatilization technique agree with independent analyses of standard rock samples (Marshall and Hess, 1958a) and with the results by neutron activation (Table 1), equilibration of the spike and the sample lead seems to have occurred. Much of the variation in the concentration values may be real in spite of the fact that comparatively large amounts of meteorite, as used in the present experiments, would be expected to average out heterogeneities.

Independent observations also suggest that variations of lead and related elements do occur within a meteorite. Reed *et al.* (1958) observed that the lead

concentration in three comparatively small (1·5 g) samples of Holbrook varied by a factor of 2, while the thallium values differed by a factor of 10. The greatest thallium concentration did not occur in the piece containing the most lead. The bismuth content differed by a factor of 4 among the same samples. These investigators also found that the concentration of thallium in different samples of the Modoc chondrite varied by a factor of 4. The values for the amount of lead in Holbrook that were calculated from the data of EDWARDS and HESS (1956) varied by a factor of 2 (cf. Table 1, footnote †).

Variations in the isotopic composition of lead from samples of the same meteorite would also be expected on the basis of significant differences in the amount of lead in different parts of the meteorite. In the preceding section, three different values for Pb^{208}/Pb^{204} from portions of the Nuevo Laredo achondrite were mentioned. Two quite different isotopic analyses for the chondrite Richardton have been found. In spite of the considerable uncertainty of the first analysis (that for Richardton (a)), these values do not seem to be compatible with those of the second set (Richardton (b)). Similarly, the differences among the Holbrook analyses seem to be outside experimental error. Although the Holbrook-N (b) sample could have been contaminated by a small amount of Pb^{206}-rich spike lead used in the concentration determinations, the high value for α in that analysis may be a natural variation. In general, differences in isotopic composition appear to accompany variations in the concentration of lead within a meteorite.

Lead–lead ages and uranium–lead and uranium–thorium ratios

The lead–lead age determinations for stone meteorites may be questioned from the standpoint of the fundamental assumptions involved in the calculations, as well as possible errors in analysis. Nevertheless, the formal calculations of the ages and the geochemical ratios can serve for comparison with independent observations. In particular, the geochemical ratios

$$\mu_1 = \frac{Pb^{204}}{U^{238}} \quad \text{and} \quad \kappa_1 = \frac{Th^{232}}{U^{238}}$$

which are calculated from the isotopic composition of the lead, and which are the relative amounts of these elements which should be present today in the stone meteorite, can be conveniently compared to the observed concentrations of lead, uranium and thorium. All of these quantities are presented in Table 6. The calculations are based on PATTERSON's (1955) corrected and averaged analyses of lead from troilite in two iron meteorites.

Although the lead–lead ages (Table 6) vary from about 4·3 to 4·6 Æ, most of them lie very close to the isochron for 4·6 Æ, as shown in Fig. 1. This diagram is in good agreement with the observations of PATTERSON (1956). The most radiogenic leads (Richardton, see Table 4, and Nuevo Laredo) significantly have ages of 4·6 Æ. The smallest percentage of error should be involved in the calculations for these two meteorites.

For three meteorites—Richardton, Beardsley and Forest City—the ratios of uranium to lead (μ_1 values in Table 6) calculated from the isotopic compositions of the lead are similar to the ratios (μ_2) based on the observed concentrations.

Table 6. Lead-lead ages and geochemical ratios computed from the isotopic compositions of lead from chondrites*

Sample	Pb–Pb age (Æ)	μ_1 (calculated from isotopic composition of lead)	μ_2 (from measured concentrations)†	κ_1 (calculated from isotopic composition of lead)	κ_2 (from measured concentrations)†‡
Richardton (a)	$4{\cdot}6_9$	$17_{\cdot 13}$	$9_{\cdot 5}$	$4{\cdot}3_2$	$3{\cdot}1_9$
Richardton (b)	4·61§	>28	$23_{\cdot 8}$	3·70§	
Holbrook-N (a)	$4{\cdot}6_8$	$7{\cdot}6_2$	2·6	4·83	$3{\cdot}0_9$
Holbrook-M 1	4·54	$7{\cdot}1_1$		3·51	
Holbrook-M 2	4·48	$6{\cdot}6_0$		2·68	
Beardsley	4·27	$4{\cdot}5_0$	4·5**	2·27	$4{\cdot}4_5$**
Plainview	4·58	$5{\cdot}2_6$	(1·4)††	3·43	—
Forest City	4·50‡‡	9·80‡‡	7·4	3·97‡‡	$3{\cdot}8_5$
Average crustal lead	4·51	9·18§§	—	4·07§§	—

* The lead-lead age ω has been calculated from the following equations:

$$\alpha = \alpha_\omega + \mu_1[\exp \lambda_1\omega) - 1] \quad \text{where} \quad \mu_1 = \frac{U^{238}}{Pb^{204}} \text{ today, calculated}$$

$$\beta = \beta_\omega + \mu_1\varepsilon[\exp (\lambda_2\omega) - 1] \quad \text{where} \quad \varepsilon = \frac{U^{235}}{U^{238}} \text{ today}$$

$$\gamma = \gamma_\omega + \mu_1\kappa_1[\exp (\lambda_3\omega) - 1] \quad \text{where} \quad \kappa_1 = \frac{Th^{232}}{U^{238}} \text{ today, calculated}$$

$$\mu_2 = \frac{U^{238}}{Pb^{204}} \text{ observed} \qquad \kappa_2 = \frac{Th^{232}}{U^{238}} \text{ observed}$$

Values of the physical constants used for the calculations in Table 6 and Appendix B:

$\lambda_1 = 0{\cdot}153_{69}Æ^{-1}$
$\lambda_2 = 0{\cdot}972_{16}Æ^{-1}$ } Fleming *et al.* (1952).

$\lambda_3 = 0{\cdot}0488_{13}Æ^{-1}$} Senftle *et al.* (1956).

$\varepsilon = \frac{1}{137{\cdot}7}$ } Senftle *et al.* (1957).

$\alpha_\omega = 9{\cdot}50$
$\beta_\omega = 10{\cdot}36$ } Patterson (1955).
$\gamma_\omega = 29{\cdot}49$

† With uranium concentrations of Hamaguchi *et al.* (1957).
‡ With thorium concentrations of Bate *et al.* (1959).
§ Calculated from ratios corrected for estimated contamination.
** Uranium concentration = 0·011 p.p.m. (Reed, 1958).
†† Based on only one lead concentration measurement. Average uranium content for chondrites (0·011 p.p.m.) assumed.
‡‡ From isotopic composition given by Patterson (1955).
§§ After Marshall (1957). The slight differences in the values for μ and κ in the above table from the ones published in 1957 are because of the slightly different sets of values for the physical constants.

For Richardton this comparison is quite approximate, as the lead concentration is uncertain by a factor of 2. The agreement in the case of Beardsley may be fortuitous for the same reason; however, its lead concentration seems to be more reliable.

Forest City may have a slight excess of radiogenic lead. If the isotopic composition of this chondrite is actually more radiogenic than reported by PATTERSON (1955), the discrepancy will be greater. PATTERSON does not describe the size of

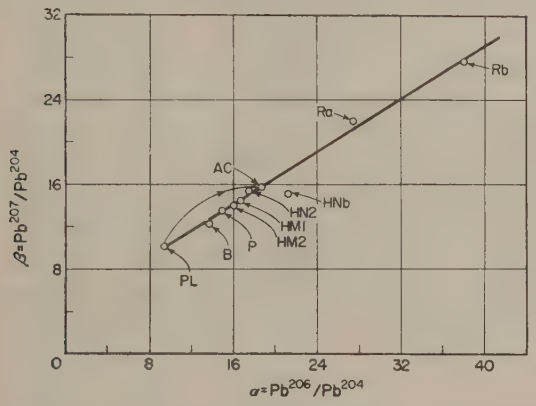

FIG. 1. α–β Diagram for Lead from Chondrites. PL indicates primeval lead (PATTERSON, 1955), and AC is average modern crustal lead (MARSHALL, 1957). Other letters designate meteorites referred to in the text and in Table 4. [E.g., Rb refers to the (uncorrected) isotopic composition of lead found in our second analysis of the Richardton chondrite.] The solid straight line is the isochron for 4·6 Æ. The curved line represents the evolution of lead in the crust of the earth.

the samples; but, presumably, he used larger samples to separate lead for isotopic composition measurements than to determine concentrations. If the contamination per experiment did not vary appreciably, the isotopic compositions would not be affected by contamination to the extent implied by the concentration measurements.

It is probably significant that the leads reported for both Forest City and Modoc by PATTERSON (1955), and also that reported for Modoc by EDWARDS and HESS (1956), are more radiogenic than average terrestrial lead. These leads generally seem to occur in chondrites with less than 0·1 p.p.m. of lead, in concordance with the nearly uniform uranium concentrations observed by HAMAGUCHI *et al.* (1957). Instead of 0·3 p.p.m. of lead, the meteorite Mocs (EDWARDS and HESS, 1956) may contain less than 0·1 p.p.m.

In Table 6 the thorium–uranium ratio calculated from the isotopic compositions varies from surprisingly low values near 2 to values over 4. Of course, the lower values will have an exaggerated error if the primeval ratio Pb^{208}/Pb^{204} (i.e. γ_ω) is not correct. Where the difference $\gamma - \gamma_\omega$ is small, as in Beardsley, κ_1 will be considerably too small if γ_ω is too large. Recent analyses of the lead from the Canyon Diablo iron meteorite (MARSHALL and HESS, 1960) show that γ_ω may be no more than about 29·0 in contrast to the presently accepted value of 29·49 given by PATTERSON (1955). This lower value would raise some of the smallest values of κ_1 to about 3 and only slightly affect those which are larger. In any case, the average value for κ_1 for stone meteorites seems to be between 3 and 4. The average of the ratios (κ_2) for the measured concentrations of uranium and thorium is also in this range. The thorium-to-uranium ratio in the crust of the earth (MARSHALL, 1957) appears to be higher than in meteoritic material.

The radiogenic lead from thorium (Pb^{208}) appears to be nearly 50 per cent deficient in Beardsley (cf. $\mu_1\kappa_1/\mu_2\kappa_2$ in Table 6). The analysis for thorium in Beardsley is 25 per cent higher than the average of 3·85 p.p.m. (mean deviation, $\pm 0{\cdot}05$) for four other chondrites (Bate *et al.*, 1959). Although Beardsley has more caesium (Gordon *et al.*, 1957) and about 20 per cent more potassium than the average chondrite (Edwards and Urey, 1955), the uranium content of this meteorite is the same as that of other chondrites (0·011 p.p.m.; Reed, 1958). The value for thorium in Beardsley (Bate *et al.*, 1959) is probably not typical and may be another example of the heterogeneity of the chondrites. With a quarter less thorium, κ_2 becomes $3{\cdot}5_9$. By changing γ_ω as indicated in the preceding paragraph, κ_1 becomes 2·74 and $\mu_1\kappa_1/\mu_2\kappa_2$ is much nearer unity. There is probably very little imbalance between the lead and thorium in Beardsley.

Holbrook contains about 0·3 p.p.m. of lead. This concentration is several times as large as those observed in a number of other chondrites. In addition, the isotopic composition of the lead in Holbrook is only a little less radiogenic than that of average modern terrestrial lead. There seems to be at least 2·5 times as much radiogenic lead as should be present. This factor is not so great as those implied by Patterson's (1955) measurements for Forest City and Modoc, but it does seem to be well outside experimental error. It should also be emphasized that this conclusion is based on the analyses of three different samples of the Holbrook fall. This discrepancy complicates the interpretation of the lead–lead age of this chondrite.

Summary

The conclusions which may be drawn from the data presented in this paper, together with other investigations of meteorites, are as follows:

(1) The amounts of lead in typical chondrites differ by a factor of over 2. Lead, caesium and bismuth (all occurring in concentrations of less than 1 p.p.m.), and probably some of the other easily fractionated elements have concentrations that vary appreciably, in contrast to the nearly uniform concentrations of other elements, particularly uranium and thorium. Thus, the isotopic composition of lead in a chondrite can approach that in troilite; or, at the other extreme, it can be much more radiogenic than modern average terrestrial lead.

(2) The lead–lead ages from the most radiogenic meteoritic lead are, significantly, 4·6 Æ. This is presumably the time at which the gross separation of iron from silicates occurred within the solar system.

(3) The concentration of lead in Holbrook is several times as great as can be accounted for on the basis of the uranium content of the meteorite and the isotopic composition of its lead and that of primeval lead.

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Appendix A
Treatment of Chondrites before Crushing

Chondrite	Approximate size and condition	Mechanical treatment of surface	Chemical treatment of surface
Richardton*	896 g; one end had been sawn off; most of the remaining surface covered with fusion crust.	Surface ground off with a new Norton Crystalon wheel; seemed softer than Holbrook-N and Forest City-1.	Rinsed several times with dil. acid followed by distilled H_2O.
Holbrook-N*	175 g; with fusion crust.	Surface ground off with a new Norton Alundum wheel.	Rinsed several times with dil. HCl, then once with conc. HCl followed by rinsings with distilled H_2O.
Holbrook-M 1†	138 g; complete fusion crust.	Only label numbers chipped off with a steel chisel.	Rinsed several times with dil. HNO_3 then once with conc. HNO_3, followed by rinsings with distilled H_2O (see Table 5 for isotopic analyses of Pb recovered in acid rinsings).
Holbrook-M 2†	141 g; complete fusion crust.	Fusion crust chipped off with a steel chisel.	None
Beardsley‡	60 g in several pieces; some fusion crust.	Only small label ground off with a diamond wheel.	Same as for Holbrook-M 1, except surface Pb not recovered.
Plainview§	A 100 g piece was with difficulty broken off a 1 kg sample of this thoroughly indurated find.	None	Successively *leached* with aqua regia until no more Pb could be dissolved from surface (see Table 5 for isotopic analyses of Pb leached from surface).
Forest City-1‡	90 g.	Surface ground off with a new Norton Crystalon wheel.	Rinsed several times with dil. HCl followed by distilled H_2O.
Forest City-2**	14 g of crushed sample (no fusion crust included) from which larger pieces of Fe had been removed.		

* Obtained from Dr. H. H. Nininger, Sedona, Arizona. This piece of Holbrook was collected about 25 years after its fall.

† Provided by Dr. B. H. Mason, American Museum of Natural History. He believes that these pieces were collected shortly after their fall.

‡ Provided by Prof. H. C. Urey, University of Chicago.

§ Provided by Dr. E. Anders, University of Chicago.

** Provided by Dr. C. C. Patterson, California Institute of Technology.

Appendix B

Lead–Lead Ages and Geochemical Ratios Computed from the Isotopic Compositions of Lead from Chondrites (from Table 3 and Text)

(Not corrected for contamination)

Chondrite	Pb–Pb age (Æ)	μ_1*	κ_1†
Richardton (a)	$4{\cdot}6_8$	$15._{73}$	$4{\cdot}3_0$
Richardton (b)	4·58	28·05	3·63
Holbrook-N (a)	$4{\cdot}6_8$	7·70	4·77
Holbrook-M 1	4·53	7·41	3·61
Holbrook-M 2	4·48	7·05	3·00
Beardsley	4·38	5·80	3·10
Plainview	4·57	5·69	3·55

* $\mu_1 = U^{238}/Pb^{204}$ today, calculated.
† $\kappa_1 = Th^{232}/U^{238}$ today, calculated.

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The absolute abundance of the chromium isotopes in chromite*†

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Abstract—Isotopic assays have been made on the chromium in eighteen chromite samples from countries responsible for 81 per cent of the chromite production between 1900 and 1950. The use of mixtures of separated isotopes to determine the accuracy indicates that the measurements are absolute. On the basis of these assays, the natural abundances of the chromium isotopes in atoms per cent are:

$$Cr^{50} = 4{\cdot}352 \pm 0{\cdot}024,$$
$$Cr^{52} = 83{\cdot}764 \pm 0{\cdot}036,$$
$$Cr^{53} = 9{\cdot}509 \pm 0{\cdot}027,$$
$$Cr^{54} = 2{\cdot}375 \pm 0{\cdot}018.$$

where the limits cited represent 3σ. No variation in the isotopic composition of the chromium in any of the chromites examined was found within the stated limits.

The chemical atomic weight, computed on the basis of these abundance values and the latest accepted values for the masses of the involved isotopes, is $51{\cdot}998_5 \pm 0{\cdot}001_3$.

Chromium is one of the elements on which no systematic study of the isotopic abundances has been made with regard to the geological source of the materials used in the study. All the results of previously reported work were obtained with chemical reagents taken from the usual stores of these materials. As is evident in Table 1, there is no real agreement among any of the results.

According to W. H. Hartford‡ the main supply of modern chromium chemicals available in this country is from the chromite deposits in the Union of South Africa. Thus, it appears that the variation of the results listed in Table 1, with the exception of those of Aston, may be due to fractionation brought about in the chemical processing of the ores or by natural geological processes; or, they may be due to unknown discriminations involved in the various instruments with which the measurements were made.

With this in mind, a study was made of the abundances of the Cr isotopes in samples of chromite and other chromium bearing minerals collected from well-characterized deposits throughout the world. The present paper reports the results of the initial studies dealing with the primary mineral, chromite. Descriptions are given of the precautions taken to eliminate instrumental discriminations and the development of a technique by which highly precise measurements can be made with this and the other transition elements. A report of the studies on secondary chromium minerals will be given in a subsequent publication.

Table 2 lists eighteen chromite specimens obtained from countries responsible for 81 per cent of the chromite ore produced from 1900 to 1950 (Udy, 1956).

* Contribution no. 785. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

† Presented at the Geochemistry Symposium of the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.

‡ Private communication, 2 November 1955. (Mutual Chemical Company, Baltimore, Maryland.)

Table 1. Previous determinations of the abundances of the chromium isotopes, in atoms per cent (Bainbridge and Nier, 1950)

Measurement / Ion source reagent observer	1 Gas discharge $Cr(CO)_6$ Aston	2 Thermionic Cr metal Nier	4 Electron impact $CrCl_3$ White, Cameron	4 Electron impact $CrCl_3$ Hibbs
Isotope 50	4·9	4·49	4·31 ± 0·04	4·41 ± 0·06
Isotope 52	81·6	83·77	83·76 ± 0·14	83·46 ± 0·11
Isotope 53	10·4	9·55	9·55 ± 0.09	9·54 ± 0·06
Isotope 54	3·1	2·31	2·38 ± 0·02	2·61 ± 0·09

Table 2. Source and type of chromite used in this study*

Ore number	Location of deposit	Remarks
1	Tiebaghi, New Caledonia	Red ore
2	Fantoche, New Caledonia	Grey ore
3	Acoje or Zambales, Philippines	
4	Rustenberg, Western Transvaal	
5	Lydenberg, Eastern Transvaal	
6	Western Transvaal	Exact location unspecified
7	Transvaal	
8	Rhodesia	Great Dyke, 190 miles NNE of Selukwe, concentrates from alluvial deposits
9	Rhodesia	Great Dyke, 150 miles NNE of Selukwe, friable lump
10	Elazig Province, Turkey	Guleman ore from near Erganimaden
11	Ural Mountains, Russia	Russian chrome, several possible locations
12	Angelita, Cuba	Concentrates of Holquin ore
13	Black Lake, Quebec	Recent operation
14	Black Lake, Quebec	Concentrates
15	Black Lake, Quebec	Old sample from early operations at Black Lake
16	Hartford County, Maryland	Near Cooktown
17	Texas, Pennsylvania	
18	Benbow, Montana	Concentrate

* The ore samples were collected with the cooperation and assistance of Dr. W. H. Hartford, Mutual Chemical Co., Baltimore, Maryland and Drs. C. Roy and D. Biggs of the Geology Dept., Iowa State University of Science and Technology, Ames, Iowa.

Experimental

In a previous publication (Flesch and Svec, 1958) a preparation of chromyl fluoride by vacuum distillation from a solid–solid mixture of CrO_3 and CoF_3 was described. The high vapour pressure of chromyl fluoride and its convenient preparation made this compound ideal as a means of introducing the element into the mass spectrometer as a gas, which affords the experimenter the advantage of extremely stable sample conditions. To avoid any possibility of introducing errors because of possible isotopic effects on the fragmentation (Schaeffer, 1953)

of this compound, $CrO_2F_2^+$ ions were chosen as the ion currents on which to base each abundance determination. The anisotopic nature of fluorine simplified the handling of the mass-spectrometric data.

Since considerable chemical manipulation is required to convert chromite ores to CrO_3, a simpler procedure for preparing CrO_2F_2 was sought. In the course of this search, experiments revealed that the CrO_3 used in the above method could be replaced by lead chromate. This greatly simplified the conversion of the ores to chromyl fluoride, since the element could be readily separated as lead chromate from the leachings of chromite–sodium peroxide fusions. To accomplish this, the ores were finely pulverized, fused with an excess of sodium peroxide, and leached with distilled water. The leachings were neutralized with glacial acetic acid, filtered to remove the silica, and then solid lead acetate was added to precipitate the chromium as lead chromate. Excess reagents were used throughout to ensure complete separation of the chromium, thus avoiding any possible isotopic fractionation effects during the chemical treatment. The lead chromate was filtered, washed, air dried, and then ignited at from 400 to 500°C (Duval, 1953) to remove any residual organic matter as well as to dry the material. The ignited lead chromate was immediately placed in a dry box, where it was stored until used. For conversion to chromyl fluoride the lead chromate was finely ground and intimately mixed with an excess of CoF_3. The mixture was placed in a copper reaction tube. Bronze turnings were placed above the charge to prevent blow-over of the reactants during subsequent evacuation of the reaction tube.

The reaction tube was removed from the dry box and attached to the remainder of the sample preparation apparatus. The assembled sample preparation apparatus consisted of a $\frac{1}{4}$ in. copper reaction tube which was about 6 in. long, a $\frac{1}{4}$ in. copper U-tube, and a packless, bellows-type valve (Hoke M482). The components were joined by means of standard flare fittings, and the assembled apparatus was attached to the inlet system of the mass spectrometer through a stainless steel fitting (Hoke S24). An aluminium gasket was used to make the latter connection vacuum tight.

A furnace was placed about the reaction tube and the temperature was raised to 375°C. This initial heat served to outgas the reactants and reaction tube without any loss of chromyl fluoride since the fluorination reaction does not proceed at this temperature. The outgassing was accompanied by an increase of pressure which was monitored by the inlet vacuum system Pirani gauge. When the pressure had returned to near normal, a dry-ice–trichloroethylene slush was placed about the U-tube to trap the chromyl fluoride, and the furnace temperature was increased to 550°C. Again the pressure in the inlet vacuum system increased due to oxygen produced during the fluorination of the lead chromate. When the pressure had returned to normal, the reaction was considered complete. The furnace was removed, and the chromyl fluoride was then treated like any other condensable gas. Samples of this compound could be stored in the copper container for several days without any apparent deterioration.

The mass spectrometer employed in the study was a 180° instrument of 5 in. radius (Consolidated Electrodynamics Corporation, Model 21–220, modified in this laboratory). A 200 μA current of 70 V electrons ionized the chromyl fluoride at

an analyser pressure of less than 5×10^{-7} mm Hg, indicated by an ionization gauge placed within 12 in. of the ion source. The vacuum system was arranged to give differential pumping. Preliminary experiments to determine the optimum instrumental operating conditions were performed using a reference sample of chromyl fluoride prepared from lead chromate, which had been prepared from reagent-grade chromic bromide. This chromyl fluoride was assayed over the complete mass range of the instrument and found to be 99^+ per cent pure with the principal impurity being HF.

Other experiments showed that the sensitivity of the mass spectrometer for the $CrO_2F_2^+$ ions was constant in the ion accelerating voltage range of from 1600 to 1700 V. This meant that the isotopic $CrO_2F_2^+$ ion currents could be voltage scanned in that range, which was more convenient than magnetic scanning. It was found that the most reproducible results were achieved when the $CrO_2F_2^+$ ions were manually scanned to obtain the desired mass spectrograms. Ten spectrograms were made by scanning the mass region 120–124 in alternate directions. Consecutive spectrograms were averaged, which resulted in nine sets of data for each assay of any particular chromyl fluoride sample.

The oxygen isotopes could not be ignored in any isotope determination using $CrO_2F_2^+$ ions, since ion currents at masses 121, 125 and 126 were observed and their magnitudes agreed with those calculated for ions containing O^{17} and O^{18}.

Since direct measurement of the oxygen isotopes in CrO_2F_2 was not possible, an indirect measurement was made. Since the production of chromyl fluoride involved the fluorination of $PbCrO_4$ by means of CoF_3, some means of examining directly the abundance of the oxygen isotopes in this chromate was sought. The most direct procedure developed involved the reaction of lead chromate with potassium fluobromite, $KBrF_4$, according to the method of Sheft *et al.* (1956). The liberated molecular oxygen was introduced directly into a dual collector, 60°, 6 in. radius mass spectrometer and the O_2^{34}/O_2^{32} and O_2^{33}/O_2^{32} ratios measured. Atmospheric oxygen, for which Nier (1950) gives an absolute ratio for O_2^{34}/O_2^{32} of 0·00409, was used as a comparison standard in order to place all measurements on an absolute basis.

All of the $PbCrO_4$ samples prepared from the ores listed in Table 2 and the distilled water at Iowa State University were examined. The results of the $KBrF_4$ fluorinations along with that of CoF_3 are summarized as follows:

	O_2^{33}/O_2^{32}	O_2^{34}/O_2^{32}
1. $PbCrO_4 + KBrF_4 \overset{400°C}{\rightleftharpoons} O_2 + \ldots\ldots$	0·000730 ± 5	0·003930 ± 5
2. $H_2O + KBrF_4 \overset{25°C}{\rightleftharpoons} O_2 + \ldots\ldots$	0·000730 ± 5	0·003930 ± 5
3. $PbCrO_4 + CoF_3 \overset{550°C}{\rightleftharpoons} O_2 + \ldots\ldots$	0·000730 ± 5	0·003930 ± 5

From these results it appeared that the oxygen in the $PbCrO_4$ was derived primarily from the distilled water used to leach the sodium peroxide–chromite fusions and to wash the precipitated lead chromate. To ensure that fractionation of the oxygen isotopes did not occur during the fluorinations one experiment was performed in

which four different samples of O_2 were collected at various times during the reaction. Assay of this gas gave identical results with those already cited.

An exchange experiment designed to confirm the nature of the exchange between CrO_4^{2-} and H_2O^{18} was performed. Vacuum-dried sodium chromate was dissolved in water enriched in O^{18} to 5 atom per cent. As soon as complete solution was achieved the water was distilled off and crystalline Na_2CrO_4 recovered. After being dried in vacuum at 70°C for 7 hr this material was fluorinated with $KBrF_4$. (In this case the fluorination proceeded smoothly at 200°C.) Measurement of the O_2^{34}/O_2^{32} ratio for the evolved oxygen indicated complete exchange within the short time of the experiment. This is essentially in agreement with the results of Brodskii and Dontsova (1940) and of Mills (1940) whose measurements of the oxygen isotopes were based on the density of the water employed.

On the basis of these results it was concluded that correction of the observed $CrO_2F_2^+$ ion currents for the oxygen isotopes had to be based upon the observed abundances in the distilled water supply at Iowa State University. Accordingly corrections of the observed ion currents were made on the basis of $O^{16}/O^{17} = 2740$, and $O^{16}/O^{18} = 508{\cdot}9$ for the oxygen isotopes in the distilled water and the assumption that the oxygen in chromyl fluoride was a random collection of oxygen atoms. Thus the calculated abundances of the O^{16}, O^{16}; O^{16}, O^{17}; and O^{16}, O^{18} combinations were 99·536, 0·073, and 0·391 per cent, respectively. Any other combinations were present to less than 0·001 per cent and were considered negligible.

The equations which relate the observed ion currents to the abundances of the chromium isotopes are:

$$M^{120} = A^{50} \tag{1}$$

$$M^{122} - 0{\cdot}00393\, A^{50} = A^{52} \tag{2}$$

$$M^{123} - 0{\cdot}00073\, A^{52} = A^{53} \tag{3}$$

$$M^{124} - 0{\cdot}00073\, A^{53} - 0{\cdot}00393\, A^{52} = A^{54}, \tag{4}$$

where M is the observed ion current, A is the relative abundance, and the superscript is the isotopic mass number. The factors 0·00073 and 0·00393 are the ratios $O^{16},O^{17}/O^{16},O^{16}$, and $O^{16},O^{18}/O^{16},O^{16}$, respectively. A simplification which introduced negligible error was the replacement of the terms A^{52} and A^{53} in the left hand members of the equations (3) and (4) with M^{122} and M^{123}, because the products of the decimal fractions involved were negligible. Thus equations (1) to (4) were reduced to:

$$M^{120} = A^{50} \tag{5}$$

$$M^{122} - 0{\cdot}00393\, M^{120} = A^{52} \tag{6}$$

$$M^{123} - 0{\cdot}00073\, M^{122} = A^{53} \tag{7}$$

$$M^{124} - 0{\cdot}00073\, M^{123} - 0{\cdot}00393\, M^{122} = A^{54} \tag{8}$$

which were used in all the subsequent treatment of the data.

Since there was small probability of obtaining equal ion currents for all eighteen samples of chromyl fluoride, the reference sample of chromyl fluoride was assayed at one-half, at normal, and at twice the normal operating pressure to determine whether or not the assays were pressure dependent. The results of this experiment

are shown in Table 3. They indicate that no pressure effect on the assays occurred and that the electrometer tube input resistor was truly ohmic in its behaviour.

Comparison of the assays of the chromyl fluoride prepared from the eighteen chromite ores depended on the stability of the instrument during the period required to assay the materials and the absence of any fractionation effects during the production of the CrO_2F_2 and its subsequent volatilization into the inlet system of the mass spectrometer. Accordingly, three different check experiments were devised. The first check involved chromyl fluoride made from commercial

Table 3. Isotope assay of chromyl fluoride at various pressures
(Isotope abundance, atoms per cent)

Isotope	50	52	53	54
Half normal pressure	4·335	83·768	9·529	2·368
Normal pressure	4·332	83·759	9·535	2·373
Twice normal pressure	4·343	83·760	9·524	2·372

Table 4. Instrument stability. (Isotope abundance, atoms per cent*)

Mass	A	B	C
50	4·347 ± 0·005	4·353 ± 0·005	4·347 ± 0·003
52	83·754 ± 0·016	83·760 ± 0·008	83·760 ± 0·005
53	9·515 ± 0·009	9·515 ± 0·007	9·521 ± 0·005
54	2·384 ± 0·005	2·372 ± 0·003	2·372 ± 0·004

* All variations cited are the standard deviations.

CrO_3 and assayed four different times during a 12 day period. The second and third checks involved different chromyl fluoride preparations from lead chromate which had been made from reagent-grade chromic bromide. In the second check, two samples of chromyl fluoride, made from different portions of the lead chromate, were assayed 5 days apart. In the third check, an additional preparation was assayed four times during a 5 day period. Thus all fractionation or discrimination possibilities were considered. The average assay and single standard deviation of each check are shown in Table 4 in columns A, B and C, respectively. These results indicated that comparison of the assays of the eighteen ore samples could be made with no concern about day-to-day instrumental drift or chemical fractionation effects.

Another potential error involved the exact nature of gas flow in the mass spectrometer. The sample inlet system of the instrument was equipped with a viscous leak which consisted of a 5 in. length of copper capillary tubing of 0·005 in. internal diameter terminated by an adjustable constriction. Differential pumping in the ion source indicated the probability that mass discrimination due to effusive flow was present. However, it has been shown that the nature of the correction factor that should be applied to isotope measurements for this and other instrumental discriminations is dependent upon the detailed physical conditions existing

in a particular mass spectrometer (Junk and Svec, 1958). It is therefore most reliable to determine these correction factors by calibration of the instrument by means of mixtures of separated isotopes.

Mixtures of separated chromium isotopes were first considered for this calibration. Thus the calibration would have been made with the same species as those used in the measurements. Preparations of 99·8% Cr^{52} and 96·5% Cr^{53} were obtained from the Oak Ridge National Laboratory. Attempts to use CrO_2F_2 prepared from mixtures of these materials were fruitless due to an inability to assay the separated isotopic materials satisfactorily with the instrument at hand. This was principally the result of an exchange between the chromium of the chromyl fluoride and the chromium of the Nichrome V used in the construction of the ion source. This exchange resulted in assay errors whose magnitude depended on the difference of the sample composition from that of normal chromium. For samples whose isotopic abundances were normal, errors from this effect were computed to be negligible. The difficulty might have been circumvented by constructing a new source of some other material or gold plating the existing source. Both of these possibilities were considered and the latter was seriously contemplated. This will be done for the extension of the work to secondary chromium materials where the preliminary experiments indicate differences in the isotopic constitution.

A compromise calibration for the present phase of the work was accomplished with a mixture of separated nitrogen isotopes which was carefully prepared and assayed according to the method described by Junk and Svec (1958) to produce absolute abundance values.* This mixture was then assayed with the mass spectrometer employed throughout the chromium studies under conditions in which the range of ion acceleration voltage was as nearly identical as possible with those under which the chromium assays were made. The value obtained here for the nitrogen isotope mixtures was 42·29 atom per cent N^{15} compared to 42·18 obtained by Junk. However, the indicated agreement to one part in 423 was obtained only when the data were corrected for fractionation due to effusive gas flow from the ion source. A correction factor equal to the square root of the inverse ratio of the masses involved had to be applied. Because the precision obtained in this calibration approached that obtained with the chromium measurements, it was safe to assume that all of the mass discrimination due to gas flow could be considered to be the result of effusion of the sample material from the ion source.

After these preliminary experiments, the samples of chromyl fluoride prepared from the eighteen chromite ores were assayed along with the reference sample during a 2 week period. The observed data for the ores were first corrected for gas flow discrimination and then for the oxygen isotope effect. The results are listed in Tables 5 and 6. Table 5 gives the individual assays of the eighteen samples and the average assay. Table 6 gives the standard deviation associated with each individual assay and the average of the eighteen individual standard deviations.

Comparison of the results listed in Tables 5 and 6 shows that the standard

* The assistance of G. Junk in this preparation and absolute assay is gratefully acknowledged.

Table 5. Isotope abundance determination of the chromite ores
(Isotope abundance, atoms per cent.)

Isotopes / Samples	50	52	53	54
1	4·357	83·763	9·497	2·373
2	4·348	83·774	9·506	2·371
3	4·357	83·757	9·506	2·379
4	4·350	83·748	9·522	2·380
5	4·351	83·764	9·511	2·374
6	4·347	83·781	9·505	2·368
7	4·348	83·771	9·510	2·371
8	4·357	83·750	9·496	2·388
9	4·357	83·764	9·500	2·379
10	4·353	83·754	9·515	2·378
11	4·346	83·769	9·509	2·377
12	4·348	83·759	9·514	2·379
13	4·346	83·762	9·515	2·377
14	4·352	83·764	9·509	2·374
15	4·347	83·759	9·519	2·376
16	4·348	83·767	9·512	2·373
17	4·352	83·771	9·508	2·369
18	4·362	83·767	9·502	2·369
Ave.	4·352	83·764	9·509	2·375
σ	0·006	0·009	0·007	0·005

Table 6. Standard deviation associated with each abundance determination of the chromite ores shown in Table 5.
(Standard deviation $\times$ 1000.

Isotopes / Samples	50	52	53	54
1	10·1	8·8	5·3	4·7
2	3·8	6·7	5·0	3·1
3	9·4	10·9	12·5	4·0
4	2·6	6·0	4·6	2·3
5	4·8	9·0	3·9	3·5
6	4·2	10·2	4·2	4·5
7	2·6	5·5	5·6	3·4
8	5·7	9·6	4·2	3·9
9	3·3	6·0	3·2	2·9
10	2·4	3·8	3·6	2·0
11	5·7	7·9	4·4	3·8
12	3·1	7·3	2·6	3·5
13	10·5	11·6	5·6	3·7
14	2·1	6·7	5·3	4·5
15	2·4	13·6	13·8	3·6
16	3·5	9·7	8·5	3·1
17	3·8	8·1	3·7	5·0
18	10·3	14·7	7·2	3·4
Ave.	5·0	8·7	5·7	3·6

deviation from the average assay of the eighteen ores was nearly identical to the average standard deviation associated with each individual assay. It must therefore be concluded that there is no variation in the isotopic composition of chromium with respect to the source of chromite ore. In order to examine the statistics of the determinations further, every individual datum from each of the assays was grouped into a composite of 170 items for each isotope abundance. The standard deviation of the composite data is larger but is more reliable than

Table 7. Composite of all data for chromite ores

Mass	Abundance (%)	Standard ± deviation	Number of items outside 3 σ limit
50	4·352	0·008	2
52	83·764	0·012	0
53	9·509	0·009	0
54	2·375	0·006	1

that of the average assay of the eighteen ores, because in the calculation of the latter, the standard deviation for each individual assay was ignored.

Despite the good precision of the data above, it was necessary to consider whether or not the values obtained represented the absolute abundances of the chromium isotopes and were not merely relative values. The results of the previously mentioned experiments, which were designed to measure and correct for discrimination effects due to gas flow, voltage scanning, variation in gas pressure, non-ohmic electrometer input resistors, impure sample gases, and instrumental drift, led the writers to assume that the resulting measurements were absolute.

Summary

Chromite ores gathered from various deposits throughout the world were assayed for the abundances of the chromium isotopes. No differences in the relative abundances were observed.

Upon application of criteria to determine the absoluteness of the measured abundances of the isotopes of chromium, the only discrimination observed during the measurements was that due to effusive gas flow out of the ionizing region of the ion source. The magnitude of this discrimination was determined from measurements of a mixture of separated nitrogen isotopes and corrections were made for it. On this basis, the abundances of the chromium isotopes reported in this communication can be considered absolute. Since chemical chromium has a common source, it is conservative to accept these absolute abundance values for the isotopes in reagent chromium. At the $\pm 3\sigma$ level (99·7 per cent confidence level), the recommended values in atoms per cent are:

$$Cr^{50} = 4{\cdot}352 \pm 0{\cdot}024$$
$$Cr^{52} = 83{\cdot}764 \pm 0{\cdot}036$$
$$Cr^{53} = 9{\cdot}509 \pm 0{\cdot}027$$
$$Cr^{54} = 2{\cdot}375 \pm 0{\cdot}018$$

Using these values and the most recently published and accepted values for the masses of the chromium isotopes (DUCKWORTH, 1958), a value for the chemical atomic weight (conversion factor = 1·000275) of $51{\cdot}998_5 \pm 0{\cdot}001_3$ has been obtained wherein the stated uncertainty combines the effects of both mass and abundance measurements and is computed by conventional statistical methods.

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